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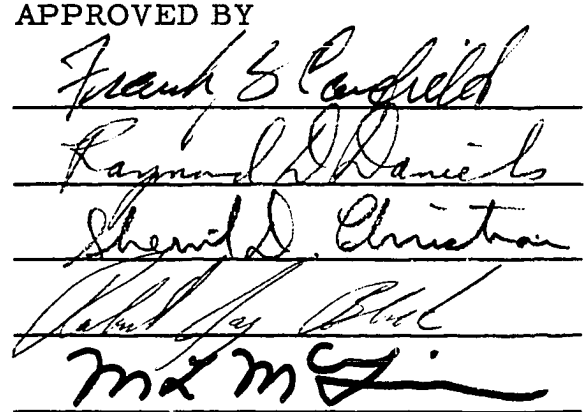

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ABSTRACT

Mathematical relationships are developed for binary diffusion to show: (1) Fick's second law should be applied only to systems which have constant partial molal volumes, (2) the equivalence of the mutual diffusion coefficients in the center of moles and center of volume systems, and (3) Darken's equations can be derived without the restriction of constant or equal partial molal volumes. It is shown that Fick's diffusion equation can be used to obtain binary diffusion coefficients from experimental data for either the volume or mole reference frame as long as the specific volume of the mixture follows a linear law over the concentration range employed.

Mutual and self diffusion coefficients were obtained for the liquid cadmium-lead system over the entire composition range at 623 K. The capillary reservoir technique was used employing Pb-210 and Cd-115m as tracers. The self diffusivities were found to be in agreement with data reported previously by Mirshamsi. Both isotopes were used to study the effect of overall concentration on the mutual diffusion coefficient. Several improvements in the capillary reservoir technique, which were necessary before mutual diffusivities could be obtained using this method, are described.

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DIFFUSION IN LIQUID METALS

CHAPTER I

INTRODUCTION

Diffusion in single phase binary solutions is considered in this work; no attempt is made to treat solutions containing more than two components. Three types of diffusion coefficients exist for a binary system: (1) mutual - D_{AB} and D_{BA}, intrinsic - D_A and D_B and self - D_A^* and D_B^*. Almost without exception the two mutual diffusivities must be equal, i. e., either component of a binary can be designated as component A. However, each component in a binary solution has a self and an intrinsic diffusivity. In general all three types are functions of concentration, temperature and pressure.

The mutual diffusivity gives an indication of the rate at which composition gradients are dissipated. The self diffusivity is a mobility and therefore a measure of the ability of molecules or atoms to move through the solution. The intrinsic diffusivity is defined with reference to Darken's (7) inert markers and is used as a mathematical crutch in relating the self diffusivities to the mutual diffusivity. Robinson (20)

points out that when an intrinsic diffusivity is defined relative to a mass or volume fixed reference frame it is a simple function of the mutual diffusion coefficient and not a separate entity.

Darken (7) proposed the following equation to relate the self and mutual diffusivities,

$$D_{AB} = (X_A D_B^* + X_B D_A^*) \frac{d\ln a}{d\ln X} \quad . \tag{1}$$

This equation was developed for metallic solids and the existing data seem to substantiate its validity. Nothing in the derivation of Darken's equation limits it to solids, and it has been applied to organic liquid systems. The results indicate that the equation is valid for ideal solutions but not for nonideal systems. No previous test of the relationship has been made for liquid metals.

Rathbun (19) has proposed an empirical equation similar to Darken's which he claims is valid for organic liquids containing one associating component,

$$D_{AB} + (X_A D_B^o + X_B D_A^o) \left(\frac{d\ln a}{d\ln X}\right)^s . \tag{2}$$

D_A^o and D_B^o are constants and are evaluated at the extremes of concentration. The exponent on the thermodynamic factor takes a value of 0.6 for systems deviating positively from Raoult's law and 0.3 for systems with negative deviation. The equation has been checked for several systems and was found to predict the data within experimental error.

Cullinan (6) uses a modification of the absolute rate theory based on Eyring's (11) hole model to derive the following equation,

$$D_{AB} = (D_A^o)^{X_B} (D_B^o)^{X_A} \frac{d\ln a}{d\ln X} . \qquad (3)$$

D_A^o and D_B^o are the same constants as employed by Rathbun. Vigners (22) has applied this equation to most of the diffusion data available with very promising results. It successfully predicts the data for nonassociating systems, including nonideal organic liquids and metallic solids, but fails for associating systems.

Because of the approximate nature of these equations they cannot be extended to different systems unless substantiated by data. Liquid metal systems are examples. The difficulty associated with taking these data have discouraged intensive investigation, but the increasing importance and use of liquid metals now demands greater efforts along these lines.

The method employed in this work to obtain diffusion data was the capillary-reservoir technique (1), utilizing radioactive isotopes as tracers. In this method, self diffusivities are determined by measuring the decrease in radioactivity of a capillary after it has been allowed to diffuse into a reservoir of the same composition but containing no radioactive atoms. Mutual diffusivities are determined by measuring the change of radioactivity of a capillary that has been allowed to diffuse into a reservoir of a different concentration. In this case, both the

capillary and the reservoir contain radioactive matter with the ratio of the active atoms being the same as the ratio of the concentrations.

The self and mutual diffusion coefficients were determined for the liquid cadmium-lead system at 350°C. Mirshamsi (18) previously determined the coefficients for this solution for a range of temperatures that bracketed 350°C. His self diffusion measurements are valid and have been verified by this study. But, in measuring the mutual diffusivity he erred in that radioactive atoms were not included in the reservoir. Since the deviation from Darken's equation of Mirshamsi's final data was similar to many organic systems, only experimental data could prove or disprove his method of determining the mutual diffusion coefficient.

The theoretical goal of this research was, of course, to develop the theory of diffusion and subsequently of the liquid state. The fruits were (1) a better understanding of Fick's second law by showing it to be an ideal solution law and (2) the removal of the restriction of constant or equal partial molal volumes from Darken's equation.

The experimental goals consisted mainly of measuring diffusion coefficients for a liquid metal system and determining the limitations of the capillary-reservoir technique in measuring mutual diffusivities in the mid-composition range. Also a check of Mirshamsi's method was needed. All these goals have been fulfilled and are discussed in Chapters IV and V.

CHAPTER II

THEORY

Fick's Laws

In 1855 Adolph Fick (10) laid down the basis for the study of atomic transport of matter. Two diffusion laws are attributed to him. His first law is the definition of a diffusion coefficient,

$$J_A = - D_{AB} \nabla C_A, \tag{4}$$

and states that the flux of component A (or B) is proportional to the negative of the concentration gradient. Consideration of unsteady state diffusion leads to Fick's second law,

$$\frac{\partial C_A}{\partial t} = \nabla \cdot (D_{AB} \nabla C_A) \tag{5a}$$

and

$$\frac{\partial C_B}{\partial t} = \nabla \cdot (D_{BA} \nabla C_B). \tag{5b}$$

When utilizing Equations 5a and 5b it is most important to keep in mind that they are only mass balances or continuity equations and, as such, their proportionality constants, D_{AB} and D_{BA}, are in general not

equal. But, for general application, binary diffusion coefficients must be interchangeable, i. e., D_{AB} must equal D_{BA}. The experimentalist is then compelled to choose the conditions under which diffusion coefficients are obtained such that the coefficients will be equal.

The equality of the diffusivities in Equations 5a and 5b is now assumed, leaving only one coefficient, D_{AB}. First, the thermodynamic restrictions of this assumption will be examined and then the practical applications will be discussed. Throughout this work every equation may be assumed to be at constant temperature and pressure unless otherwise noted. The following fundamental equations are used in the development (see Appendix B for derivations):

$$\underline{V}_m = X_A \bar{V}_A + X_B \bar{V}_B, \tag{6}$$

$$C\underline{V}_m = 1 = C_A \bar{V}_A + C_B \bar{V}_B, \tag{7}$$

$$C_A = CX_A, \quad C_B = CX_B, \tag{8}$$

$$\bar{V}_A \nabla C_A + \bar{V}_B \nabla C_B = 0, \tag{9}$$

$$\nabla C_A = C^2 \bar{V}_B \nabla X_A, \tag{10}$$

and

$$\nabla C_B = C^2 \bar{V}_A \nabla X_B \,. \tag{11}$$

Multiplication of Equation 5a by $\bar{V}_A$ and Equation 5b by $\bar{V}_B$, addition and utilization of Equation 9 gives

$$\bar{V}_A \nabla \cdot (D_{AB} \nabla C_A) + \bar{V}_B \nabla \cdot (D_{AB} \nabla C_B) = 0, \tag{12}$$

which upon expansion is

$$D_{AB} (\bar{V}_A \nabla^2 C_A + \bar{V}_B \nabla^2 C_B) + \nabla D_{AB} \cdot (\bar{V}_A \nabla C_A + \bar{V}_B \nabla C_B) = 0. \tag{13}$$

The second term above is zero from Equation 9 so

$$\bar{V}_A \nabla^2 C_A + \bar{V}_B \nabla^2 CB = 0. \tag{14}$$

This is expanded to give

$$\nabla \cdot (\bar{V}_A \nabla C_A + \bar{V}_B \nabla C_B) - \nabla C_A \cdot \nabla \bar{V}_A - \nabla C_B \cdot \nabla \bar{V}_B = 0. \tag{15}$$

Because of Equation 9, the first term of Equation 15 is zero, and

$$\nabla C_A \cdot \nabla \bar{V}_A + \nabla C_B \cdot \nabla \bar{V}_B = 0. \tag{16}$$

By substituting for C_i from Equation 8 and expanding, Equation 16 is transformed to

$$C(\nabla X_A \cdot \nabla \bar{V}_A + \nabla X_B \cdot \nabla \bar{V}_B) + \nabla C \cdot (X_A \nabla \bar{V}_A + X_B \nabla \bar{V}_B) = 0. \tag{17}$$

The second term is zero because of Equation 9 and, with $\nabla X_A = - \nabla X_B$,

$$\nabla X_A \cdot \nabla(\bar{V}_A - \bar{V}_B) = 0. \tag{18}$$

Now the argument is made that either the vectors are orthogonal or $\nabla(\bar{V}_A \cdot \bar{V}_B) = 0$ for this condition to hold. They cannot be orthogonal because the partial molal volumes are functions of the mole fraction, hence the gradient of $(\bar{V}_A - \bar{V}_B)$ is zero.

Equation 6 is differentiated with respect to X_A to yield

$$\frac{\partial \underline{V}_m}{\partial X_A} = \bar{V}_A - \bar{V}_B + \left(X_A \frac{\partial \bar{V}_A}{\partial X_A} + X_B \frac{\partial \bar{V}_B}{\partial X_A} \right). \tag{19}$$

The last term of Equation 19 is zero and the rest, when substituted into Equation 18, gives

$$\nabla X_A \cdot \nabla\left(\frac{\partial \underline{V}_m}{\partial X_A} \right) = 0. \tag{20}$$

Thus it is argued that

$$\nabla \frac{\partial \underline{V}_m}{\partial X_A} = 0, \tag{21}$$

and, upon integration,

$$\underline{V}_m = k_1 X_A + k_2. \tag{22}$$

Comparison of Equations 6 and 22 leads to

$$k_1 = \bar{V}_A - \bar{V}_B \tag{23}$$

and

$$k_2 = \bar{V}_B, \tag{24}$$

and the conclusion is reached that the partial molal volumes must be constant in any application of Fick's second law. In Appendix B it is shown that any solution having constant partial molal volumes (no change of volume on mixing) for all temperature and pressure is an ideal solution. Therefore, Fick's second law is an ideal solution diffusion equation.

In the experimental determination of diffusion coefficients the solution must be ideal or the concentration interval must be small enough for the specific volume to obey a linear law (Equation 22). Two mathematical solutions to Fick's second law are used to demonstrate difficulties that may arise when using experimental data. The first is the one used in this work and is found by applying the Laplace transform technique to the following equation (see Appendix B for solution),

$$\frac{\partial C_A}{\partial Xt} = D_{AB}\nabla^2 C_A \tag{25}$$

and then integrating the results over the volume of the system to get

$$\frac{C_f - C_r}{C_o - C_r} = \frac{8}{\pi^2} \sum_{n=o}^{\infty} \frac{1}{(2n+1)^2} e^{-\left(\frac{(2n+1)\pi}{2L}\right) D_{AB}t} \tag{26}$$

The first criticism of the above solution is that the diffusivity was assumed to be a constant. The best possible results would be an average over the concentration interval.

The second case to be considered is the Boltzmann-Matano

(4, 17) solution to Equation 5a, which yields (see Appendix B for derivation)

$$D_{AB\,C_A''} = -\frac{1}{2t}\left(\frac{\partial z}{\partial C_A}\right)_{C_A''} \int_{C_o}^{C_A''} z\, dC_A \qquad (27)$$

In this case D_{AB} is determined as a function of concentration, and is therefore more realistic than the first solution.

Now, consider the worst possible example of non-ideality in the change of volume on mixing, i. e., the partial molal volume of one of the components, $\bar{V}_B$, being negative at one extreme of the concentration, going through zero and then back to pure component specific volume at the other extreme. In this case diffusion will occur against the concentration gradient when the gradient is expressed in units of moles or mass per unit volume (diffusion does not occur against the mole fraction gradient) and Equation 26 will not allow this, i. e., it blows up for component A. On the other hand, the Boltzmann-Matano solution will give a diffusivity for component A with a discontinuity at the concentration where the partial molal volume of B is zero, being positive infinity on one side and negative infinity on the other side. The diffusion coefficient determined from data on component B has no discontinuity and behaves much as is expected in both the solutions to Fick's second law. All this trouble arises from the fact that the original equation is a mass balance applicable in situations where ideal solution laws are obeyed. Negative partial molal volumes and uphill diffusion are discussed more

thoroughly in Appendix E.

No matter how small the concentration intervals in the above case, the results are the same. Use of Equation 25 requires that (1) the concentration interval be small enough so no appreciable error is introduced due to the assumption of constant diffusivity, (2) the concentration interval be small enough that the specific volume of the mixture follows a linear law and (3) neither of the partial molal volumes goes to zero. The Boltzmann-Matano solution requires that restrictions 2 and 3 be obeyed. The applicability of Fick's second law, then, depends both upon the method of measurement and the system under investigation.

Frames of Reference

In order to write mass balances or continuity equations for both components in a binary system and have the two diffusion coefficients equal, it is necessary to account for all fluxes present. Kirkwood (16) and Bird (3) present excellent discussions of frames of reference and counting methods. The diffusional flux takes a form dependent upon the reference frame chosen. The diffusional velocity is defined as

$$u_i^r = u_i - u^r, \tag{28}$$

where u_i^r is the diffusional velocity of species i relative to the reference, u_i is the velocity of i relative to a stationary coordinate and u^r is the velocity of the reference frame. The total flux is then

$$N_i = C_i u_i, \tag{29}$$

and the diffusional flux is

$$j_i^r = C_i u_i^r = N_i - C_i u^r . \tag{30}$$

For the center of moles reference frame m is substituted for r in Equation 28, 29 and 30. Also, the following equations are valid,

$$u^m = X_A u_A + X_B u_B, \tag{31}$$

$$j_A^m + j_B^m = 0 \tag{32}$$

$$C_u^m = N_A + N_B = C_A u_A + C_B u_B , \tag{33}$$

and the diffusion coefficient is defined by

$$j_A^m = C D_{AB}^m \nabla X_A . \tag{34}$$

Combination of the total flux and the diffusional flux gives

$$N_A = j_A^m - C_A u^m . \tag{35}$$

It is of interest to determine the relationship between the diffusion coefficient of the center of moles reference frame, D_{AB}^m, and Fick's diffusivity, D_{AB}. The continuity equations take the form

$$\frac{\partial C_A}{\partial t} = - \nabla \cdot N_A \tag{36}$$

and

$$\frac{\partial C_B}{\partial t} = - \nabla \cdot N_B \tag{37}$$

Multiplication of Equation 36 by $\bar{V}_A$ and 37 by $\bar{V}_B$, summation and application of Equation 9 gives

$$\bar{V}_A \nabla \cdot N_A + \bar{V}_B \nabla \cdot N_B = 0. \tag{38}$$

At this point the partial molal volumes are assumed constant and Equation 38 is integrated over the total volume of the system,

$$\int_V (\nabla \cdot \bar{V}_A N_A + \nabla \cdot \bar{V}_B N_B) dV = 0. \tag{39}$$

Utilization of Green's Theorem allows the volume integral in Equation 39 to be transformed to the surface integral,

$$\int_S (N_A \bar{V}_A + N_B \bar{V}_B) \cdot dS = 0. \tag{40}$$

If Equation 40 is to be valid for all limits, then

$$N_A \bar{V}_A + N_B \bar{V}_B = 0. \tag{41}$$

Substitution of Equation 30 into Equation 35 gives

$$j_A^m = X_B N_A - X_A N_B, \tag{42}$$

and, by Equation 41, N_B is eliminated yielding

$$N_A = C\bar{V}_B j_A^m \tag{43}$$

or

$$N_A = -\bar{V}_B C^2 D_{AB}^m \nabla X_A. \tag{44}$$

Equation 10 will simplify this to

$$N_A = -D_{AB}^m \nabla C_A. \tag{45}$$

The flux in Fick's first law is the total flux so

$$J_A = N_A = -D_{AB} \nabla C_A, \tag{46}$$

and by comparing Equations 45 and 46, it is seen that

$$D_{AB} = D_{AB}^m. \tag{47}$$

Thus, with the assumption of constant partial molal volumes, the diffusivity in the center of moles reference frame is equal to Fick's diffusivity. The result was expected since Fick's second law is an idealized law.

The center of volume reference frame has a velocity defined by

$$u^v = \bar{V}_A N_A + \bar{V}_B N_B \tag{48}$$

and a diffusion coefficient defined by

$$j_A^v = -D_{AB}^v \nabla C_A. \tag{49}$$

From Equation 30 it can be seen that the total flux has the form

$$N_A = j_A^v + C_A u^v. \tag{50}$$

When Equation 48 is substituted into Equation 50, the result is

$$j_A^v = N_A - C_A \bar{V}_A N_A - C_B \bar{V}_B N_B, \tag{51}$$

which, with the aid of Equation 7, reduces to

$$j_A^v = C_B \bar{V}_B N_A - C_A \bar{V}_B N_B. \tag{52}$$

Equation 41 is not limited to any reference frame since N_A and N_B represent the total flux relative to a fixed coordinate system; the only limitation is the constancy of the partial molal volumes. This assumption is again made and Equation 41 is applied to Equation 52. With Equation 8 this result reduces to

$$j_A^v = N_A. \tag{53}$$

Similarly it can be shown that

$$j_B^v = N_B. \tag{54}$$

Equations 53 and 54 can be equated to Fick's first law with the result that

$$D_{AB}^v = D_{AB}. \tag{55}$$

The mass balances from the center of moles and center of volume

reference frames reduce to Fick's second law for ideal solutions, and all three diffusion coefficients are equal.

The next area of interest is the relationship between the diffusivities from the center of moles and center of volume reference frames when the partial molal volumes are not constant. Equation 35 and the companion expression for component B are substituted for N_A and N_B in Equation 51 to yield

$$j_A^v = j_A^m - C_A u^m - C_A \bar{V}_A j_A^m + C_A^2 \bar{V}_A u^m - C_A \bar{V}_B j_B^m + C_A C_B \bar{V}_B u^m, \quad (56)$$

or

$$j_A^v = C_B \bar{V}_B j_A^m - C_A \bar{V}_B j_B^m - C_A u^m + C_A (C_A \bar{V}_A u^m + C_B \bar{V}_B u^m), \quad (57)$$

but, since the last term is $+ C_A u^m$,

$$j_A^v = C_B \bar{V}_B j_A^m - C_A \bar{V}_B j_B^m . \quad (58)$$

Substitution for the diffusional fluxes (j_A^v, j_A^m and j_B^m) yields

$$- D_{AB}^v \nabla C_A = - C_B \bar{V}_B C D_{AB}^m \nabla X_A - C_A \bar{V}_B C D_{AB} \nabla X_B, \quad (59)$$

which reduces to

$$D_{AB}^v \nabla C_A = D_{AB}^m \bar{V}_B C^2 \nabla X_A . \quad (60)$$

Equation 10 is applied to the right side of the above expression giving

$$D_{AB}^v \nabla C_A = D_{AB}^m \nabla C_A \quad (61)$$

or

$$D^{v}_{AB} = D^{m}_{AB}. \tag{62}$$

The expanded continuity equations from the systems under consideration take the form

$$\frac{\partial C_A}{\partial t} = \nabla \cdot (D^{m}_{AB} C \nabla X_A - C_A u^{m}) \tag{63}$$

and

$$\frac{\partial C_A}{\partial t} = \nabla \cdot (D^{v}_{AB} \nabla C_A - C_A u^{v}). \tag{64}$$

Although the reference velocities and the resulting time dependent equations are different both Equations 63 and 64 are valid mass balances and either may be used. Again it is pointed out that Fick's second law is an ideal solution law and should be used with care experimentally and should never be used as the basis for general theoretical developments.

Self Diffusion

Darken (7) defined fluxes relative to inert markers such that intrinsic diffusivities are given by

$$j_A = C_A(u_A - u) = - D_A \nabla C_A \tag{65}$$

and

$$j_B = C_B(u_B - u) = - D_B \nabla C_B \tag{66}$$

and the fluxes relative to fixed coordinates are

$$N_A = j_A + C_A u \tag{67}$$

and

$$N_B = j_B + C_B u, \tag{68}$$

where u is used to denote the velocity of the markers. From these definitons and Fick's second law, a relationship was obtained between the binary and intrinsic diffusion coefficients,

$$D_{AB} = X_A D_B + X_B D_A. \tag{69}$$

Then, with the assumption that the driving force for diffusion is the negative gradient of the chemical potential, Darken derived the relationship between intrinsic and self diffusivities. Combination of these with Equation 69 gave

$$D_{AB} = (X_A D_B^* + X_B D_A^*) \frac{\partial \ln a_A}{\partial \ln X_A}. \tag{70}$$

In deriving both Equation 69 and 70, Darken assumed that the total concentration was constant. This assumption requires the partial molal volumes to be constant and equal. Hartley and Crank (13) derived an expression relating the intrinsic diffusivities to D_{AB}^v which reduces to Equation 70 when the potential is assumed to be the Gibbs chemical potential. Carman and Stein (5) point out that the equation, when derived in this manner, has the restriction only of constant partial molal volumes.

Darken's equation is derived below without any restriction on the partial molal volumes. The center of volume reference frame is used along with the fluxes described by Darken in Equations 65-68. Equations 67 and 68 are substituted into Equation 48 to yield

$$u^v = \bar{V}_A j_A + (\bar{V}_A C_A + \bar{V}_B C_B)u + \bar{V}_B j_B, \tag{71}$$

or, utilizing Equation 7,

$$u^v - \bar{V}_A j_A - \bar{V}_B j_B = v. \tag{72}$$

This is substituted into Equation 67 and the result is equated to N_A from Equation 50. Upon collection of terms,

$$j_A^v = j_A + C_A (\bar{V}_A N_A + \bar{V}_B N_B - u^v) - \bar{V}_A C_A j_A - \bar{V}_B C_B j_B. \tag{73}$$

Note that the term in parentheses is zero by Equation 48. Now, substituting for the fluxes j_A^v, j_A and j_B, and applying Equation 7.

$$D_{AB}^v \nabla C_A = \bar{V}_B C_B D_A \nabla C_A - C_A \bar{V}_B D_B \nabla C_B. \tag{74}$$

Division by ∇C_A and application of Equation 9 simplifies the expression to

$$D_{AB}^v = \bar{V}_B C_B D_A + \bar{V}_A C_A D_B. \tag{75}$$

With the assumption that the force per atom is $(-1/N_o)(\nabla \bar{G}_A)$, the flux may be written as

$$j_A = -\frac{1}{N_o} B_A C_A \nabla \bar{G}_A. \tag{76}$$

This flux is then equated to the flux defining the intrinsic diffusivities, Equation 49 and

$$D_A \nabla C_A = \frac{B_A C_A}{N_o} \nabla \bar{G}_A . \tag{77}$$

Division by ∇C_A yields

$$D_A = \frac{B_A C_A}{N_o} \frac{\partial \bar{G}_A}{\partial C_A} , \tag{78}$$

and for component B

$$D_B = \frac{B_B C_B}{N_o} \frac{\partial \bar{G}_B}{\partial C_B} . \tag{79}$$

The above expressions for the intrinsic diffusivities are substituted into Equation 75 and

$$D_{AB}^v = \frac{\bar{V}_B C_B B_A C_A}{N_o} \frac{\partial \bar{G}_A}{\partial C_A} + \frac{\bar{V}_A C_A C_B B_B}{N_o} \frac{\partial \bar{G}_B}{\partial C_B} . \tag{80}$$

Using the definition of the thermodynamic activity

$$\partial \bar{G}_i = RT \partial \ln a_i , \tag{81}$$

the Einstein relationship (8)

$$D_i^* = k T B_i^* , \tag{82}$$

and the assumption that $B_i^* = B_i$, the above expression becomes

$$D_{AB}^v = \bar{V}_B C_B C_A \frac{\partial \ln a_A}{\partial C_A} + \bar{V}_A C_A C_B \frac{\partial \ln a_B}{\partial C_B} . \tag{83}$$

Utilizing Equations 10 and 11 and the fact that

$$\frac{\partial \ln a_A}{\partial \ln X_A} = \frac{\partial \ln a_B}{\partial \ln X_B}, \tag{84}$$

Equation 83 is transformed to

$$D_{AB}^{v} = (X_A D_B^* + X_B D_A^*) \frac{\partial \ln a_A}{\partial \ln X_A}. \tag{85}$$

The assumptions made in deriving Equation 85 are now reviewed:

1. Constant temperature and pressure
2. $j_i = - D_i \nabla C_i$
3. $j_i = - \frac{1}{N_o} B_i C_i \nabla \bar{G}_i$
4. The fluxes in assumption 2 and 3 are equal
5. $B_i = B_i^*$
6. $D_i^* = k T B_i^*$.

Nothing is apparent in these assumptions limiting the application of Darken's equation to one physical state as apposed to another (liquid, solid, or gas). Also the equation is phenomenological and, therefore, not limited to a mechanism or model.

CHAPTER III

EXPERIMENTAL EQUIPMENT AND PROCEDURE

Diffusion Equipment

The diffusion equipment consisted of a constant temperature bath, diffusion cell, vacuum system and hydrogen gas system. Essentially the same equipment was used previously by Mirshamsi (18) and has been described in detail in his thesis; therefore only a brief description is given here.

Houghton's Draw Temp 275, contained in an eight inch diameter by fifteen inch deep stainless steel pot, was used as the heat transfer medium in the constant temperature bath. The primary heat source was a Nichrome wire heater around the outside of the pot. The temperature control was achieved with a Bayley Precision Temperature Controller connected to a 250 watt coiled immersion heater inside the pot. The temperature was sensed by a chromel-alumel thermocouple calibrated against a platinum resistance thermometer. The thermocouple potential was measured on a Leeds and Northrup No. 8662 potentiometer. Temperature variation during any diffusion run was less than $0.1^{\circ}C$.

The diffusion cell consisted of a 2-1/4 inch diameter pyrex

tube approximately 18 inches long. The tube was sealed at one end and a Dresser coupling was attached to the open end. A flange was welded to the top of the coupling and a flat plate was screw pressed against the flange. A Viton O-ring formed a vacuum tight seal between the top plate and the flange. The capillary support rod and a thermocouple well passed through O-ring seals attached to the top plate. The gas inlet and outlet were 1/4-inch copper tubes soldered into the top plate. The melted alloy was contained inside the pyrex tube in a graphite crucible. Two synchronous motors were attached to the top of the capillary support rod--one for vertical positioning and the other for rotating the capillaries. Rotation was necessary to keep the concentration at the mouth of the capillaries at the reservoir concentration.

Either a Welch Duo Seal or a Cenco Hyvac vacuum pump was used to evacuate the cell. An excessive amount of time was required to reduce the pressure below 50 microns because rubber tubing was used in part of the system. However, a pressure of 50 microns was sufficiently low to fill the capillaries.

Welding grade hydrogen was used to maintain a reducing atmosphere in the cell. Prior to being introduced to the cell the hydrogen was passed through a Deoxo catalitic reactor to remove the oxygen and then through a calcium sulfate dryer to remove the water formed in the reactor. A critical hydrogen flow rate existed below which oxides formed and the flow rate was maintained above this value. The critical

rate was determined by placing a piece of lead in the cell and observing it as the temperature was raised. At very low flow rates the lead oxidized and exhibited the characteristic bluish color. The flow rate was then increased until the lead regained its metallic luster.

Capillaries

Two types of capillaries were used in this study--glass and graphite. Precision bore pyrex tubing purchased from Corning Glass was used for the first 48 capillaries. The glass was cut into lengths of approximately one inch and one end was sealed with the inside bottom surface being nearly flat. The open end of each capillary was ground flat and then polished until it appeared smooth under a low power microscope. During grinding and polishing the capillaries were mounted in a plastic block to insure that the axis was normal to the surface. All glass capillaries had an inside diameter of $2 \pm .0025$ mm with an outside diameter of roughly 4 mm. The length of the capillaries was measured to the nearest thousandth of an inch with a depth gauge.

The two types of holders used for the glass capillaries are shown in Figure 1. Type A were used initially, but the top portion of the alloy solidified first and voids were created when the bottom portion solidified. Upon reheating the voids usually disappeared but on occasion they remained the same size or even expanded pushing some of the molten alloy out of the capillary. The type B holder allowed the alloy to solidify more uniformly and did, in fact, decrease the incidence of voids.

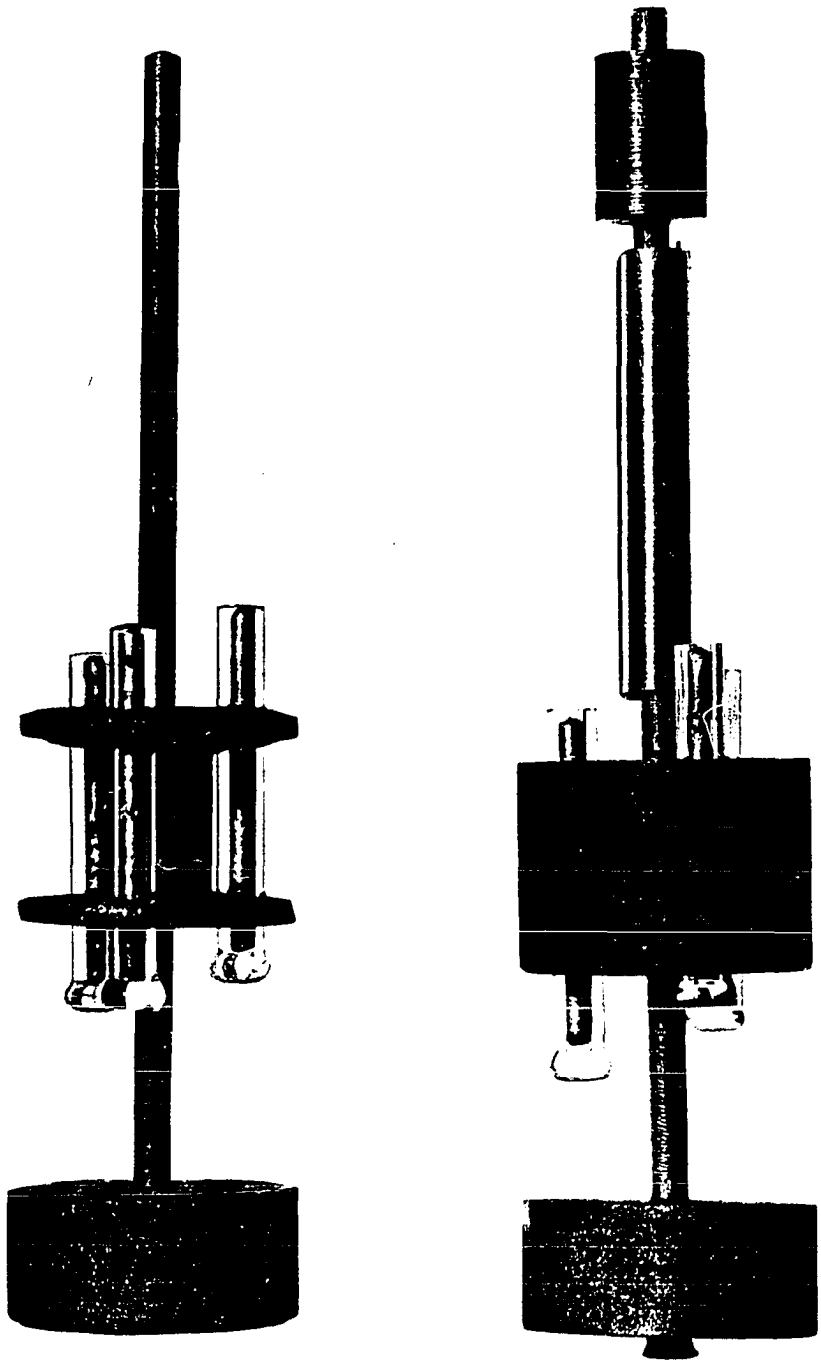

Figure 1. Holders for Glass Capillaries

In determining the mutual diffusion coefficient the count rate of the reservoir must be known accurately. To ascertain this, capillaries were filled from the reservoir and the count rate determined. The values obtained were useless unless the original capillary and the one used for the reservoir were the same length, which was generally not the case. Therefore, the count rate per unit length was used. This method was still not satisfactory because the individual capillaries gave different count rates per unit length. That the counts per unit length were not constant for a given concentration was thought to be due to the following: 1) the capillary walls did not have uniform thickness and the count rate is proportional to amount of material between the source and the detector, 2) the capillaries were not always filled to the same level, 3) the amount of glass melted during the sealing of one end of the capillaries varied thus varying the vertical positioning in the scintillation crystal, and 4) end effects arising from the capillaries being open at one end and covered at the other end.

The second reason above was eliminated by smoothing the top of each capillary after filling and after the diffusion run. When the capillaries were removed from the molten reservoir a bead of liquid metal protruded above the mouth of the capillary. In the past it had been the practice to shake the capillary holder thus knocking the beads off. This was a random process with the final liquid level being quite often either too low or too high. Therefore, a stainless steel device

(Figure 2), attached to the thermocouple well, was moved horizontally across the capillary mouth shearing the liquid at a constant level. The reproducibility of the count rate was improved considerably by the smoothing operation but was still not satisfactory. Finally the glass capillaries were discarded and graphite capillaries used.

The graphite capillaries are illustrated in Figure 2 along with the smoothing device. Three holes were drilled and then reamed to 5/64-inch at 120^{o} separation near the edge of a roughly one inch long by 3/4-inch diameter graphite cylinder. Another shorter cylinder was pressed against the bottom to act as a seal. After the holes were filled in the same manner as the glass capillaries, the device was taken apart and the alloy removed for counting. The alloy was reinserted into the graphite for the diffusion run and removed again for the final count. This method was used for the remaining portion of the data and was found to be more reproducable than the glass capillary method.

Occasionally, when the capillaries were removed from the reservoir, the liquid level in one or more of the capillaries was below its mouth. This phenomenon occurred with both types of capillaries but was more prominent for the graphite. It was found that if the capillaries were removed rapidly this did not occur as often. Therefore, at the end of a diffusion run, the vertical positioning motor was disconnected and the capillaries raised by hand. When a capillary was not full after a run, it was discarded and the data was not reported. This

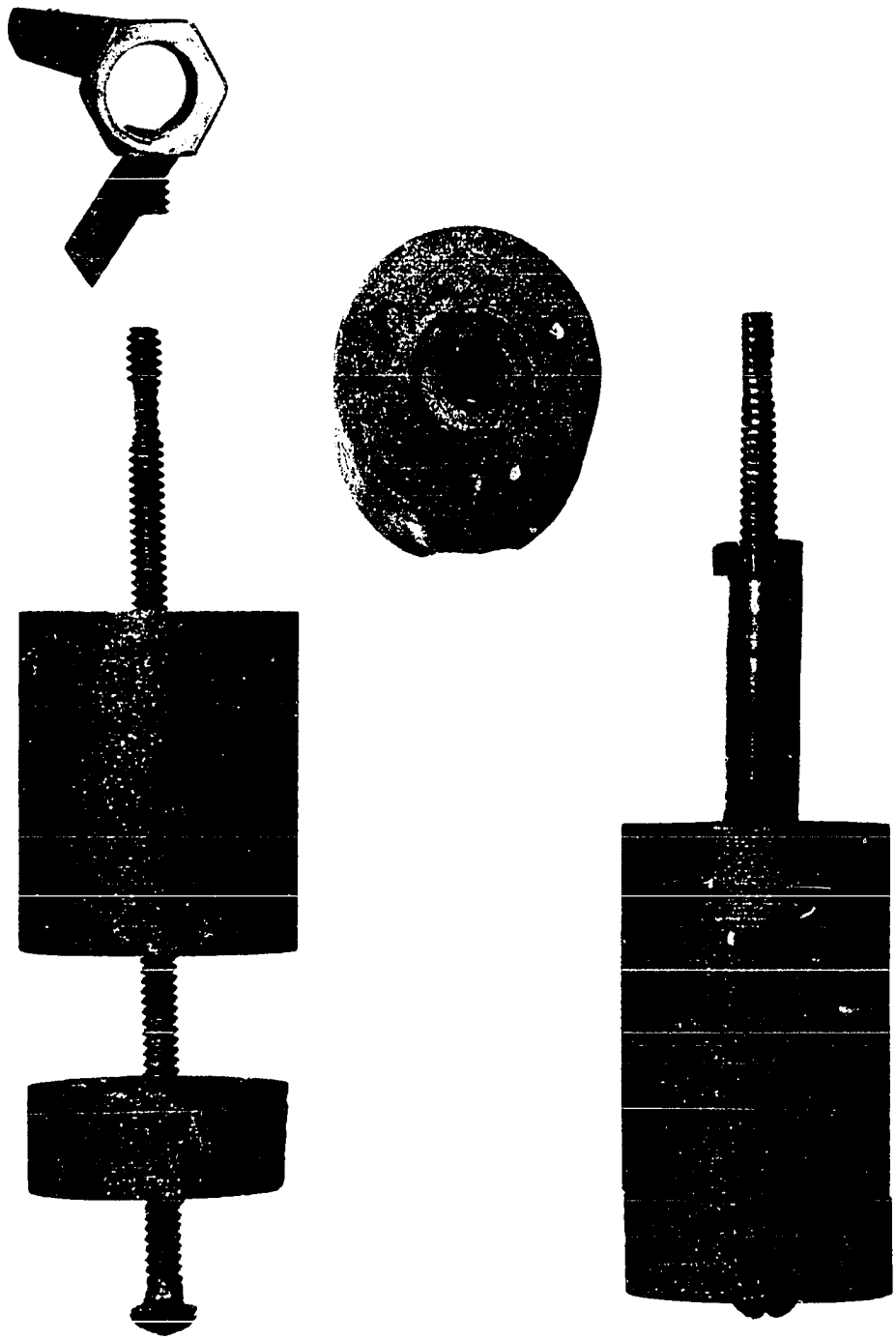

Figure 2. Graphite Capillaries and Smoothing Device

problem illustrates one of the basic shortcomings of the capillary reservoir technique--mixing effects upon entry to and exit from the reservoir.

Isotopes

The radioactive lead was received as the nitrate in a nitric acid solution. It was diluted with inactive lead nitrate and then treated with sodium carbonate to precipitate lead carbonate. This was dissolved in a solution of fluoboric acid containing excess boric acid. A small amount of animal glue was added and the active lead was electroplated from the solution onto the walls of a lead crucible. The crucible and a lead anode were cast from the high purity lead used throughout the experiment. The lead concentration in the solution remained at a constant level and the gross effect was a transfer of lead from the anode to the cathode.

The radioactive cadmium was also received as the nitrate in a nitric acid solution, diluted with the inactive nitrate and precipitated as the carbonate. The cadmium carbonate was then treated with sulfuric acid and electroplated on a high purity cadmium crucible from the cadmium sulfate solution. The above procedures are outlined by Gray (12).

The isotope counting equipment consisted of a Tracerlab model P-20CW scintillation detector, a Tracerlab RLI-4 pulse height analyzer, and either a Nuclear-Chicago model 183B or model 181A scaling unit. The counting equipment was kept in a special counting room where the temperature variations were less than the limits set by the manufacturer. The count rate varied roughly from 1, 000 to 50, 000 counts per minute.

The total counts for each sample varied from 50, 000 to 1, 000, 000.

Procedure

The metals used in this study were Cominco's 59 grade (99.999% purity). Prior to use the lead was cleaned with a 1:3 solution of 30% hydrogen peroxide and acetic acid. The cadmium was cleaned with a 10% solution of nitric acid. After cleaning, the metals were rinsed several times with distilled water and allowed to dry. The proper amounts of each were then weighed to the nearest 0. 059 and placed in the graphite crucible. The diffusion cell was assembled as usual except a graphite cylinder was substituted for the capillary holder at the bottom of the capillary support rod. This cylinder was used as a stirrer by lowering and raising it through the melted alloy. A minimum of six hours, with intermittent stirring, was allowed to insure complete mixing after every change of concentration. The cell was then allowed to cool, the graphite cylinder replaced by the capillaries, and the cell reassembled.

The cell was evacuated and checked for leaks. Then it was filled with hydrogen and the hydrogen flow rate adjusted to the proper level. The apparatus was then suspended for about 20 minutes with the bottom of the pyrex tube just above the level of the Draw Temp 275. This was done to preheat the pyrex tube thereby eliminating the possibility of breakage due to thermal stresses when it was lowered into the bath. The cell and bath were so constructed that the heat transfer medium level was about six inches above the top of the alloy in the reservoir.

After the metal had melted, the capillary holder was lowered until the liquid metal level was just below the open end of the capillaries. When the temperature of the capillaries rose above the melting point of the alloy, the cell was evacuated and the capillaries immersed in the melt. The cell was repressurized with hydrogen forcing the molten alloy into the capillaries. This operation was conducted at a temperature just above the liquidus to minimize evaporation losses during evacuation. The capillaries were left submerged in the melt until the temperature had risen to that at which the diffusion run would be made. When they were raised out of the liquid metal, the bead protruding from the top of each capillarly was skimmed off and the cell was removed from the furnace to cool.

The capillaries were removed from the cell and placed in small glass tubes for counting. Each time a set of capillaries was counted a standard sample of the same isotope and the background were also counted. The samples were then returned to the capillary holder and the cell reassembled. Again the same procedure was followed: evacuate, check for leaks, pressurize with hydrogen, warm up, and lower into the salt bath. As soon as the reservoir had melted, the capillary holder was lowered until the reservoir liquid level was just below the open ends of the capillaries. This position was maintained until the reservoir reached thermal equilibrium with the bath, i.e., the temperature ceased to change with time. Usually about 3 hours

were required to reach this temperature.

One of the synchronous motors was used to lower the capillaries into the melt until the open ends were at least one half inch below the liquid level. The other motor was used to rotate the capillaries at two revolutions per minute. At the end of the desired diffusion time, the rotation was stopped, the capillaries raised until the open ends were above the liquid level, and the beads were skimmed off. The capillaries were left in this position for several hours to allow for homogenization of the alloy in the sample. If this were not done, the final count rate did not reflect the final average concentration.

CHAPTER IV

EXPERIMENTAL RESULTS

The following quantities were measured for the cadmium-lead system: (a) self diffusion coefficient of lead in pure lead at 400°C, (b) self diffusion coefficient of lead as a function of concentration at 350°C, (c) self diffusion coefficient of cadmium as a function of concentration at 350°C, (d) mutual diffusivity as a function of concentration at 350°C using both Cd-115m and Pb-210 as tracers, (e) self diffusivities of cadmium and lead at 70.0 mass % Cd and 350°C as a function of concentration interval and (f) mutual diffusivity at 70.0 mass % Cd and 350°C as a function of concentration interval using both Pb-210 and Cd-115m as tracers.

Self Diffusion

The self diffusion coefficient of lead in pure lead was measured at 400°C to give a direct comparison with Mirshamsi's (18) data. These values are given in Table 1 and Table F-1. The remainder of Mirshamsi's data presented here are not actual data but were calculated from his smoothed curves.

TABLE I

SELF DIFFUSION OF LEAD AT 400°C

$D \times 10^5$ - cm^2/sec	
This Work	Mirshamsi
2.12	2.39
2.44	2.34
2.97	2.56
2.12	2.03
2.34	2.14
2.35	2.31
2.12	2.15
2.46	2.40
2.40	
Avg. 2.37	2.29

The lead self diffusion data are listed in Table F-2 and average values are given in Table 2. Figure 3 is a comparison of the new data Mirshamsi's. The cadmium self diffusion data are listed in Table F-3 and average values are given in Table 2. Figure 4 gives a comparison of these data with Mirshamsi's.

Mutual Diffusion

Mutual diffusivities were very difficult to obtain. The data are listed in Table F-4 for Pb-210 tracer and Table F-5 for Cd-115m tracer. Only the values for dilute solutions of each component (0-50 mass %) are presented here; the rest of the data are discussed in the last section of this chapter. A compilation of the data is given in Table 2 and shown in Figures 5 and 6. The values reported at $X_{Cd} = 0.81$ include both the

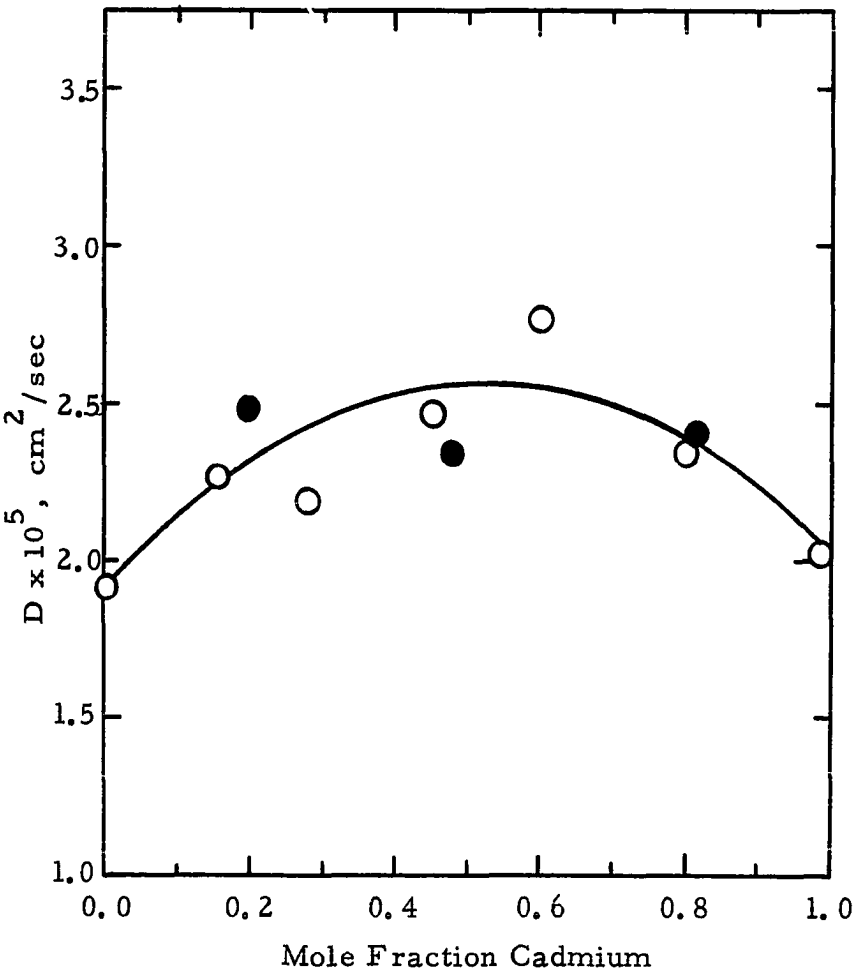

Figure 3. Lead Self Diffusion

○ Mirshamsi (18)

● This Work

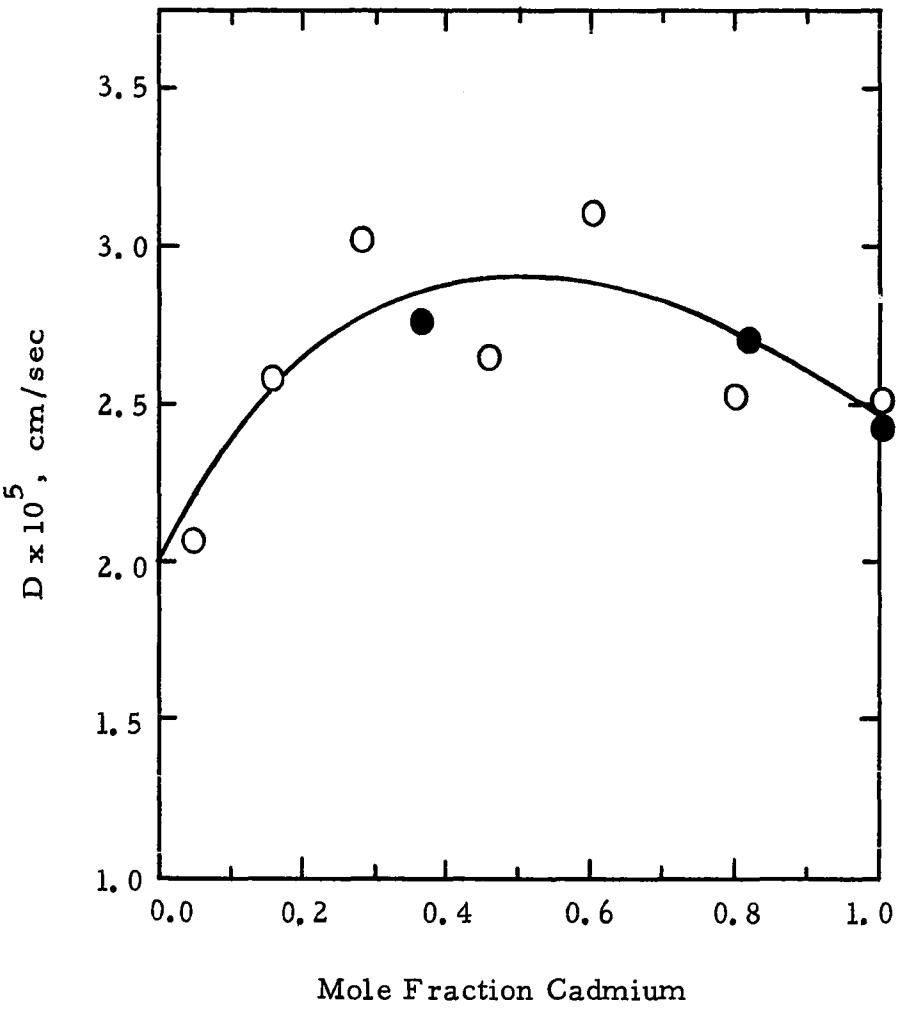

Figure 4. Cadmium Self Diffusion

○ Mirshamsi (18)

● This Work

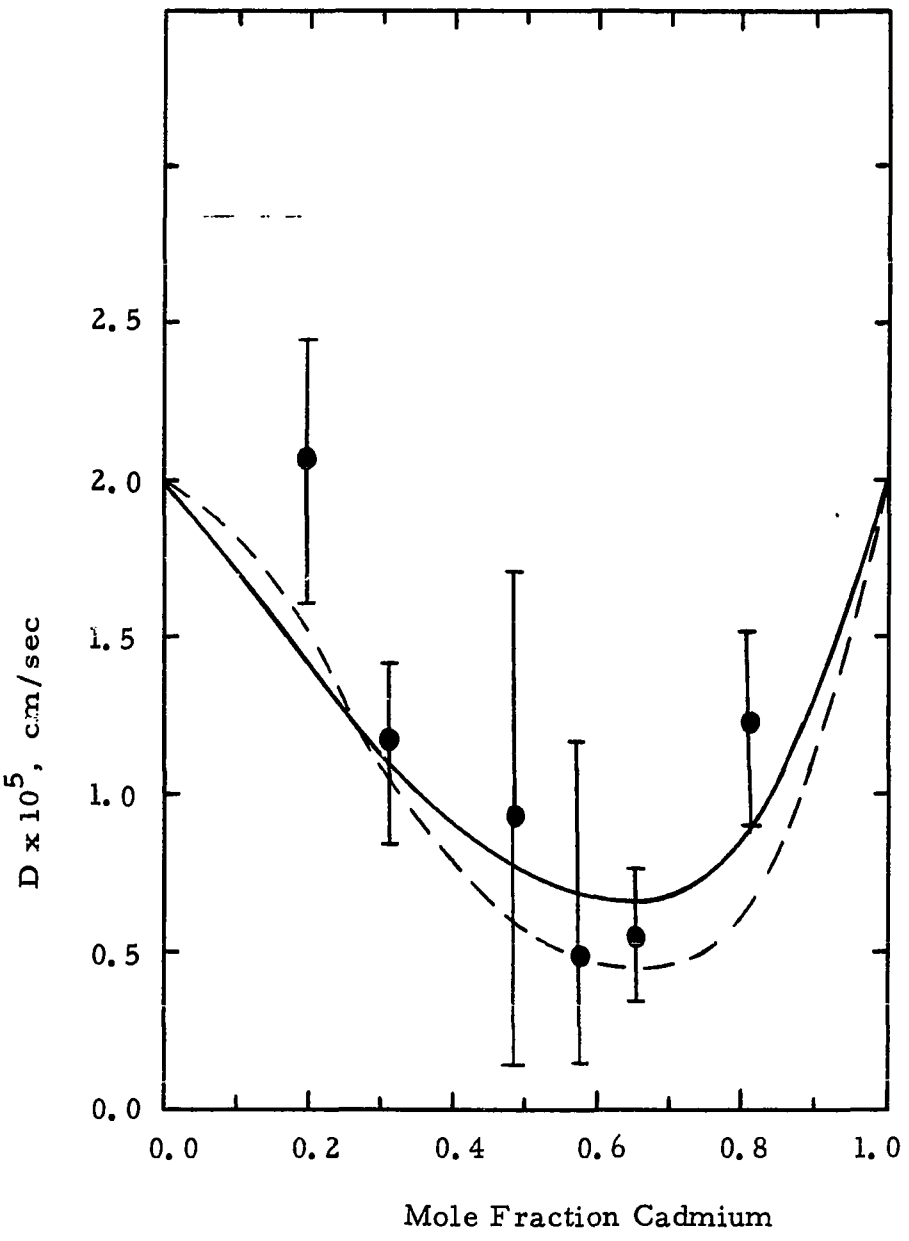

Figure 5. Cadmium-Lead Mutual Diffusion

— — — Rathbun's Equation, $D_{AB} = \left(X_A D_B^o + X_B D_A^o\right)\left(\frac{d\ln a}{d\ln X}\right)^{0.6}$

——— Darken's Equation, $D_{AB} = \left(X_A D_B^* + X_B D_A^*\right)\frac{d\ln a}{d\ln X}$

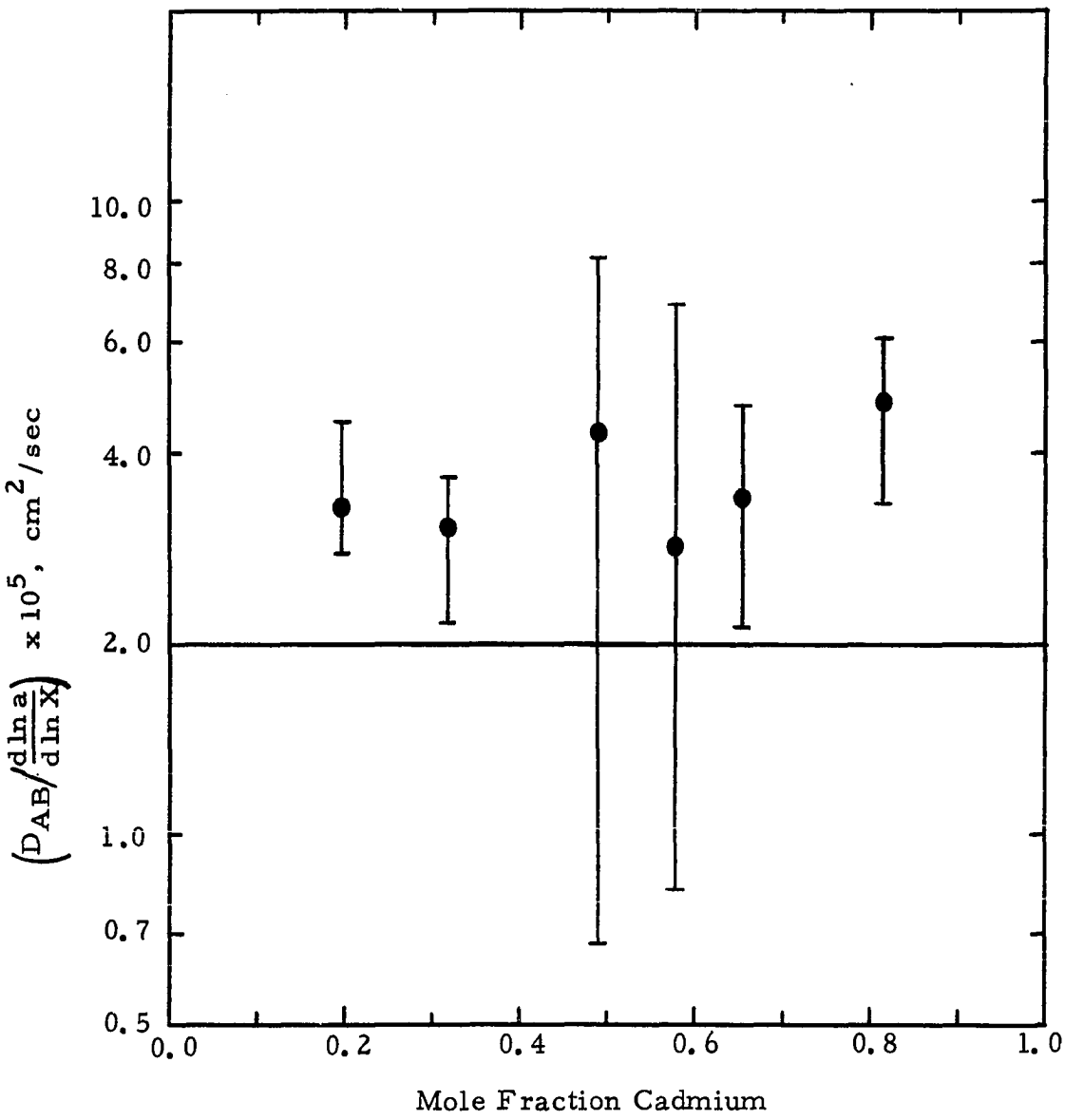

Figure 6. Comparison of Diffusion Data with Cullinan's Equation

$$\text{——} \quad D_{AB} = \left(D_B^o\right)^{X_A} \left(D_A^o\right)^{X_B} \frac{d\ln a}{d\ln X}$$

4. 02 and 8. 00 mass % Cd concentration intervals.

TABLE II

DIFFUSION DATA FOR THE CADMIUM-LEAD SYSTEM AT 350°C

X_{Cd}	$D^*_{Pb} \times 10^5$ cm^2/sec	$D^*_{Cd} \times 10^5$ cm^2/sec	$D_{AB} \times 10^5$ Cd Tracer cm^2/sec	$D_{AB} \times 10^5$ Pb Tracer cm^2/sec
.196	2. 47			
.198			2. 08	
.314			1. 19	
.367		2. 76		
.472	2. 34			
.486			.92	
.577			.49	
.652			.34	
.653				.61
.811	2. 38	2. 71		1. 22
1. 000		2. 42		

In Figure 5 comparisons of the data with Darken's equation (7) and Rathbun's equation (19) are given. A compilation of the data used to calculate these curves is given in Table 3. Figure 6 is a comparison of the data with Cullinan's equation (6).

Concentration Intervals

The self diffusion data for lead and cadmium as a function of concentration interval are given in Tables 4 and F-6 and Tables 5 and F-7 respectively. Both sets of data are illustrated in Figure 7. These data were obtained to determine the validity of Mirshamsi's method of

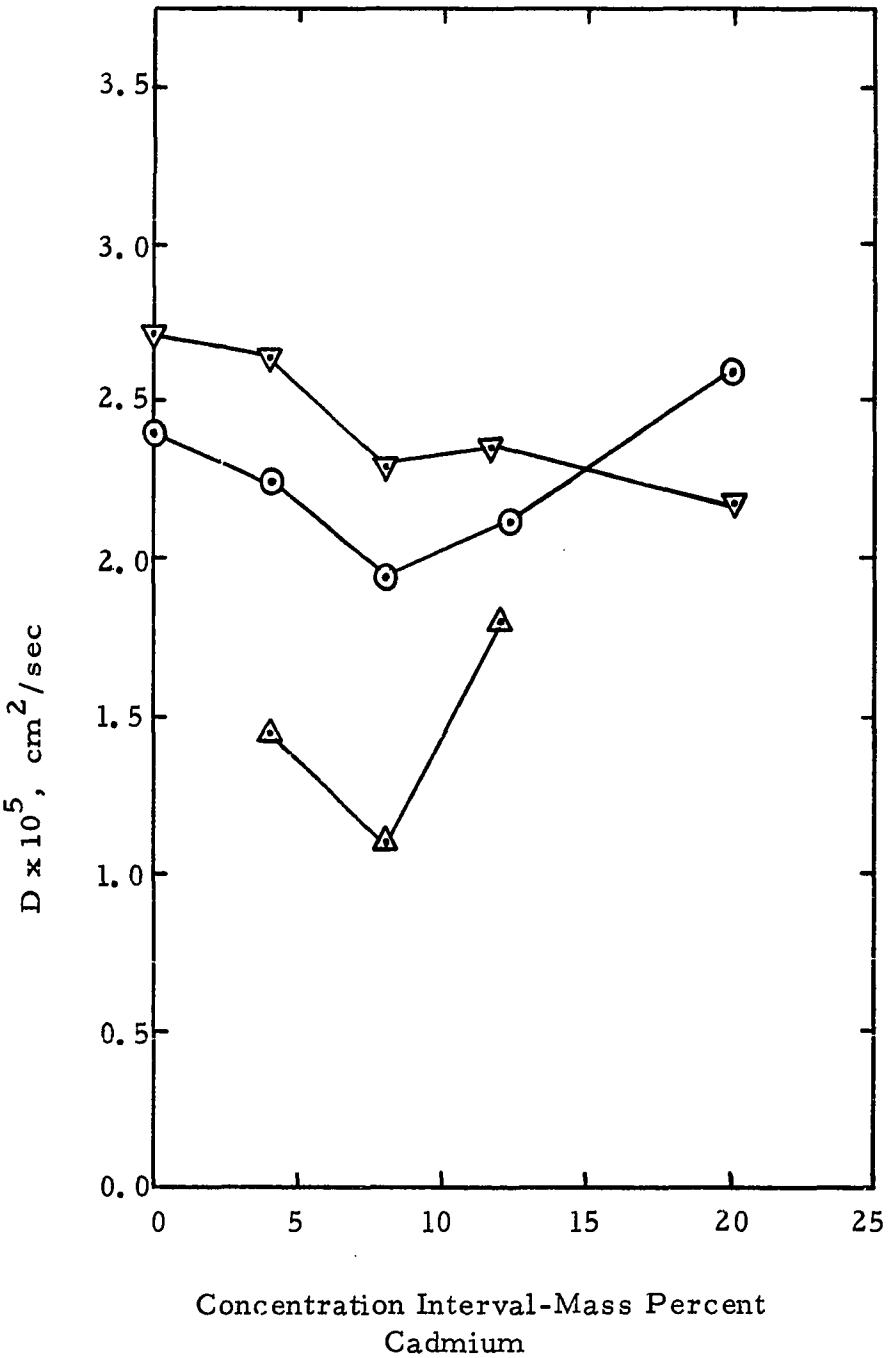

Figure 7. Diffusion Coefficients as a Function of Concentration Interval

▽ - Self Diffusion Coefficient of Cadmium
○ - Self Diffusion Coefficient of Lead
△ - Mutual Diffusion Coefficient

measuring the mutual diffusivity. He used Pb-210 to measure D_{AB} at 67.02 mass % Cd and got a value of 1.77×10^{-5} cm^2/sec. From Table 4 it can be seen that D^*_{Pb} decreased from a value of 2.38×10^{-5} for zero interval to 1.95×10^{-5} cm^2/sec for an 8% interval at 70.0 mass % Cd. Also note from Table 5 that had Mirshamsi used Cd-115m as a tracer he would have found the value of D_{AB} to be approximately 2.29×10^{-5} cm^2/sec for a 8% interval.

TABLE III

COMPILATION OF DATA; AVERAGE VALUES FROM FIGURES 3, 4 and C-2

X_{Cd}	$D^*_{Cd} \times 10^5$ cm^2/sec	$D^*_{Pb} \times 10^5$ cm^2/sec	$d\ln a / d\ln X$	$d\ln a^{0.6} / d\ln X$	(Rathbun) $D_{AB} \times 10^5$ cm^2/sec	(Darken) $D_{AB} \times 10^5$ cm^2/sec
0.0	2.00	1.91	1.00	1.00	2.00	2.00
0.1	2.39	2.14	0.78	.87	1.74	1.84
0.2	2.64	2.32	0.58	.72	1.44	1.49
0.3	2.79	2.45	0.41	.55	1.10	1.10
0.4	2.88	2.52	0.28	.47	.94	.77
0.5	2.91	2.56	0.20	.38	.76	.55
0.6	2.88	2.55	0.16	.33	.66	.43
0.7	2.83	2.49	0.17	.35	.70	.44
0.8	2.73	2.39	0.23	.41	.82	.57
0.9	2.62	2.24	0.50	.66	1.32	1.14
1.0	2.47	2.01	1.00	1.00	2.01	2.01

An attempt was made to ascertain the effect of concentration interval on the mutual diffusion coefficient. The data for Pb-210 tracer

are given in Tables 6 and F-8 and illustrated in Figure 7. The data for Cd-115m tracer are given in Table F-9 and are discussed in the next section of this chapter.

TABLE IV

LEAD SELF DIFFUSION--FUNCTION OF CONCENTRATION INTERVAL

Cadmium Concentration - mass percent			$D^*_{Pb} \times 10^5$
Capillary	Reservoir	Interval	cm^2/sec
70.0	70.0	0.00	2.38
68.0	72.0	4.02	2.25
66.0	74.0	8.00	1.95
63.9	76.1	12.28	2.12
60.0	80.0	20.04	2.59

TABLE V

CADMIUM SELF DIFFUSION--FUNCTION OF CONCENTRATION INTERVAL

Cadmium Concentration - mass percent			$D^*_{Cd} \times 10^5$
Capillary	Reservoir	Interval	cm^2/sec
70.0	70.0	0	2.71
68.0	72.0	3.98	2.63
66.0	74.0	7.95	2.29
64.2	75.8	11.62	2.36
59.9	80.0	19.96	2.17

TABLE VI

MUTUAL DIFFUSION--FUNCTION OF CONCENTRATION INTERVAL; Pb-210 TRACER

Cadmium Concentration - mass percent			$D_{AB} \times 10^5$
Capillary	Reservoir	Interval	cm^2/sec
68.0	72.0	4.02	1.44
66.0	74.0	8.00	1.09
63.9	76.1	12.28	1.81

Experimental Errors

Errors in the diffusion coefficients arises from the measurement of the following physical quantities: (a) time, (b) length of the capillaries, (c) temperature and (d) concentration.

All diffusion runs were started and stopped on the minute, plus or minus about 5 seconds. Therefore an error of $\pm$ 10 seconds or $\pm$ 0.05% is expected. The length of the capillaries was measured to $\pm$ 0.001 inch. For a one inch capillary this introduces an error of $\pm$ 0.1%. No detectable change in the temperature occurred during the entire experiment so the error due to temperature measurement is negligible.

The errors introduced in measuring the concentration arise from the following: (1) weighing the metals to make up the alloys, (2) capillaries not being exactly full, and (3) actual counting of the isotope activity. The estimated error in weighing the sample is $\pm$ 0.1% and

for the counting process $\pm$ 0.5% or less. The error introduced because the capillaries were not always filled to the same level is not known but is estimated to be less than $\pm$ 1.0%.

The error in Q, $\frac{Dt}{L^2}$, is larger than the error in the concentration ratio, $\frac{C_f - C_r}{C_o - C_r}$, and is dependent upon the magnitude of this ratio. For a $\pm$ 1% error in the ratio, Q will have a $\pm$ 7.96% error when the ratio value is 0.8 and a $\pm$ 2.02% error when it is 0.50.

An example will now be used to demonstrate the errors in the diffusion coefficient for a $\pm$ 1.0% error in the concentration. Assume that alloys are made up such that a capillary of component A has a count rate of 100,000 cpm for pure A, 50,000 cpm for 50% A and zero for zero A. Now assume, for self diffusion $C_r = 0$. For 70% A the ratio of the concentrations could be

$$\frac{C_f - C_r}{C_o - C_r} = \frac{35,000 \pm 350}{70,000 \pm 700} = 0.500 \pm .01.$$

In this case the ratio has a $\pm$ 2% error and Q has an error of $\pm$ 4%. If the diffusion time had been shorter and the ratio larger the error would be larger.

Now for the same solution, consider mutual diffusion where the initial concentration is 85%, the reservoir concentration is 75% and the final concentration is 80%. Then, for a $\pm$ 1% error,

$$\frac{C_f - C_r}{C_o - C_r} = \frac{80,000 \pm 800 - 75,000 \pm 750}{85,000 \pm 850 - 75,000 \pm 750}$$

$$= \frac{5,000 \pm 1550}{10,000 \pm 1600} = 0.500 \pm .279,$$

and the error in the ratio is $\pm$ 44%. The resulting error is Q and subsequently D_{AB} is much larger than 44%.

For mutual diffusion in the low concentration range the errors are smaller. Let the initial concentration be 15%, the reservoir be 5% and the final be 10%, and

$$\frac{C_f - C_r}{C_o - C_r} = \frac{10,000 \pm 100 - 5,000 \pm 50}{15,000 \pm 150 - 5,000 \pm 50}$$

$$= \frac{5,000 \pm 150}{10,000 \pm 200} = 0.500 \pm .0245.$$

The error in the ratio for this case is $\pm$ 4.9% and the error in Q is $\pm$ 9.15%.

As can be seen from the above analysis, mutual diffusivities can be measured in the low composition range; however, the expected error is still high. In the concentrated composition range mutual diffusivities cannot be measured. An attempt was made to measure mutual diffusivities in the concentrated range and, as expected, the results varied to such an extent that the relative worth factor to be assigned is zero. These values are reported in Tables F-4, F-5 and F-9.

CHAPTER V

CONCLUSIONS AND RECOMMENDATIONS

The conclusions reached as a result of this research are:

1. The self diffusivities agree with existing data.
2. Mirshamsi's method for measuring the mutual diffusivity is incorrect.
3. With further refinement the capillary reservoir technique could be used to measure mutual diffusivities in dilute solutions, but extension to concentrated solutions would be difficult.
4. The data have sufficient scatter so that a valid check of existing theories is impossible.

It is recommended that either a new method be found for measuring the concentrations (other than isotope tracers) or a completely new method be devised for measuring mutual diffusion coefficients.

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APPENDIX A

NOMENCLATURE

a - activity

a_i - activity of component i

A - component of a binary solution

B - component of a binary solution

B_i - mobility of component i, velocity per unit force

B_i^* - mobility of radioactive i

C - total concentration, moles per unit volume of solution

C_i - concentration of component i, moles of i per unit volume of solution

$\bar{C}_A$ - average concentration of A, defined by Equation B-36

C_A'' - concentration of A, defined by Equation B-43

C_f - final concentration

C_o - initial concentration

C_o' - initial concentration

C_r - reservoir concentration

D - mutual diffusivity with subscript omitted

D_i - intrinsic diffusivity of i, defined by Equations 65 and 66

D_i^* - self diffusivity of i

D_{AB} - Fick's mutual diffusion coefficient

D_{AB}^m - mutual diffusivity relative to the center of moles

D_{AB}^v - mutual diffusivity relative to the center of volume

D_A^o - mutual diffusivity evacuated at $X_A = 0$

D_B^o - mutual diffusivity evacuated at $X_B = 0$

E - dimensionless time, Dt/L^2

$\bar{f}_i$ - fugacity of component i in solution

$\underline{f}_i$ - fugacity of pure i

F - Faraday constant

g - a function

$\bar{g}$ - Laplace transform of g

$\underline{G}_i$ - specific Gibbs free energy of pure i

$\bar{G}_i$ - partial molal Gibbs free energy of i

H^* - specific or partial molal enthalpy at zero pressure

$\underline{H}_i$ - specific enthalpy of pure i

j_i - flux of i relative to inert markers, defined by Equations 65 and 66

J_i - flux of component i from Fick's first law

j_i^m - flux of i relative to center of moles

j_i^r - flux of i relative to r

j_i^v - flux of i relative to the center of volume

K - constant

k_1 - constant

k_2 - constant

k - Boltzmann constant

L - length

n_i - moles of i

N_i - flux of i relative to fixed coordinates

N_o - Avagadro constant

p - variable in Laplace transform

P - pressure

Q - dimensionless concentration, C_A/C_o

$\bar{Q}$ - transform of Q

R - gas constant

s - constant, defined in Equation 2

S - surface

$\underline{S}_i$ - specific entropy of pure i

$\bar{S}_i$ - partial molal entropy of i

t - time variable

T - temperature

u - velocity of inert marker

u_i - velocity

u^m - velocity of center moles

u^r - velocity of reference frame r

u^v - velocity of center of volume

u_i^r - diffusional velocity of i relative to r

U - dimensionless distance, z/L

V - volume

$\underline{V}_m$ - specific volume of mixture

$\underline{V}_i$ - specific volume of pure i

$\overline{V}_i$ - partial molal volume of i

w - same as $(-p)^{1/2}$, see Equation B-20

W - mass percent

X_i - mole fraction component i

z - distance variable

Greek letters

γ_i - activity coefficient of i, a_i/X_i

APPENDIX B

MATHEMATICAL DERIVATIONS

Derivation of Equations 9-11

The following relationships

$$\underline{V}_m = X_A \bar{V}_A + X_B \bar{V}_B, \tag{B-1}$$

$$\underline{V}_m C = 1, \tag{B-2}$$

$$dC = dC_A + dC_B, \tag{B-3}$$

$$dC_A = C\, dX_A + X_A\, dC, \tag{B-4}$$

and the Gibbs-Duhem relation,

$$\left(X_A\, d\bar{V}_A + X_B\, d\bar{V}_B\right)_{T,P} = 0 \tag{B-5}$$

are used in the development.

The result of multiplying Equation B-5 by the total concentration, C, is

$$\left(C_A\, d\bar{V}_A + C_B\, d\bar{V}_B\right)_{T,P} = 0. \tag{B-5a}$$

When Equation B-1 is multiplied by C and differentiated,

$$(C_A\, d\bar{V}_A + C_B\, d\bar{V}_B + \bar{V}_A\, dC_A + \bar{V}_B\, dC_B)_{T,\,P}. \qquad \text{(B-6)}$$

The first two terms are zero by Equation B-5a and

$$\left(\bar{V}_A\, dC_A + \bar{V}_B\, dC_B\right)_{T,\,P} = 0$$

which is Equation 9.

Equation B-3 is substituted into B-4 to yield

$$dC_A = C\, dX_A + X_A\, dC_A + X_B\, dC_B \qquad \text{(B-7)}$$

or, upon simplification,

$$X_B\, dC_A = C\, dX_A + X_A\, dC_B. \qquad \text{(B-8)}$$

Equation 9 can be used to eliminate dC_B from the above relationship, and

$$X_B\, dC_A = C\, dX_A - \left(\frac{X_A \bar{V}_A}{\bar{V}_B}\, dC_A\right)_{T,\,P}, \qquad \text{(B-9)}$$

which, upon rearrangement, becomes

$$\left(\left(X_A \bar{V}_A + X_B \bar{V}_B\right) dC_A\right)_{T,\,P} = \left(\bar{V}_B C\, dX_A\right)_{T,\,P}. \qquad \text{(B-10)}$$

Equations B-1 and B-2 are applied to the above relation to yield Equation 10

$$\left(dC_A\right)_{T,\,P} = \left(\bar{V}_B C^2\, dX_A\right)_{T,\,P}.$$

As was noted in Chapter II, the subscripts T and P were omitted to simplify the presentation. Equation 11 is derived in exactly the same manner

except the subscripts, A and B, are reversed.

Solution to Fick's Second Law

In the capillary reservoir technique for measuring diffusion coefficients, the gross effect is a transfer of mass either into or out of a capillary of length L and constant cross section. The physical quantities measured in an experiment are (1) capillary length, (2) time, (3) initial concentration in the capillary, (4) final concentration in the capillary, and (5) the reservoir concentration. (The reservoir is at least 500 times larger than the capillary thus insuring that the reservoir concentration does not change appreciably during one run.) It will be assumed that diffusion occurs at constant temperature and pressure, and that other effects (electrical, magnetic, chemical reactions, etc.) are absent. With the further assumption that diffusion is unidirectional and the diffusivity is constant, Fick's second law may be written in the form

$$\frac{\partial C_A}{\partial t} = D \frac{\partial^2 C_A}{\partial z^2} . \qquad \text{(B-11)}$$

Component A is indicated in this development, but the results are applicable to either component.

The initial and boundary conditions are:

1. the initial concentration in the capillary is C_o, or

$$C_A = C_o \qquad -L \leq z \leq 0 \qquad t < 0$$

2. after diffusion starts, the concentration at the open end of

the capillary is that of the reservoir, C_r, or

$$C_A = C_r \qquad z = 0 \qquad t > 0$$

3. the capillary is sufficiently long to insure that the gradient at the closed end is always zero, or

$$\frac{\partial C_A}{\partial z} = 0 \qquad z = -L \qquad \text{all } t.$$

The following dimensionless variables,

$$Q = \frac{C_A}{C_o}, \qquad U = \frac{z}{L}, \qquad E = \frac{Dt}{L^2},$$

are used to reduce Fick's second law to

$$\frac{\partial Q}{\partial E} = \frac{\partial^2 Q}{\partial U^2} . \tag{B-12}$$

The corresponding boundary conditions are

$$Q = 1 \qquad 0 \leq U \leq 1 \qquad E = 0, \tag{B-13}$$

$$Q = K \qquad U \leq 0 \qquad E > 0 \tag{B-14}$$

where

$$K = \frac{C_r}{C_o},$$

and

$$\frac{\partial Q}{\partial U} = 0 \qquad U = 1 \qquad \text{all } E. \tag{B-15}$$

The Laplace transform technique is then applied with respect

to dimensionless time, E, where the transform of a function g is given by

$$g = \int_0^\infty e^{-pE} g \, dE, \tag{B-16}$$

This result is integrated by parts yielding

$$\frac{d^2Q}{dU^2} = p\bar{Q} - 1. \tag{B-17}$$

The second and third boundary conditions transform to

$$\bar{Q} = \frac{K}{p} \qquad U = 0 \qquad \text{all } E \tag{B-18}$$

and

$$\frac{d\bar{Q}}{dU} = 0 \qquad U = 1 \qquad E > 0. \tag{B-19}$$

Letting

$$w^2 = -p \tag{B-20}$$

a solution of Equation B-17 is

$$Q = A \sin wU + B \cos wU + \frac{1}{p}. \tag{B-21}$$

Application of Equation B-18 at U = 0 gives

$$Q = \frac{K}{p} = B + \frac{1}{p} \tag{B-22}$$

or

$$B = \frac{K-1}{p}. \tag{B-23}$$

Application of Equation B-19 at U = 1 gives

$$\left.\frac{d\bar{Q}}{dU}\right|_{U=1} = 0 = wA\cos w - wB\sin w \tag{B-24}$$

or

$$A = B\,\frac{\sin w}{\cos w}\,. \tag{B-25}$$

Substitution of these values into Equation B-21 gives

$$\bar{Q} = \frac{K-1}{p}\left(\frac{\sin w\,\sin wU}{\cos w} + \cos wU\right) + \frac{1}{p} \tag{B-26}$$

or, reducing to the lowest common denominator,

$$\bar{Q} = \frac{K\sin w\,\sin wU + K\cos w\,\cos wU - \sin w\,\sin wU}{p\cos w} + \frac{\cos w - \sin w\,\sin wU}{p\cos w} \tag{B-27}$$

The inversion formula for Laplace transformer is

$$2\pi i Q = \int_{\gamma+i\infty}^{\gamma+i\infty} e^{pE}\,\bar{Q}\,dp \tag{B-28}$$

or, by the theorem of residues,

$$Q = \Sigma\,\text{Residues} \tag{B-29}$$

The residues are found by evaluating the integrand of Equation B-28 at the poles

$$p = 0 \tag{B-30}$$

and

$$\cos w = 0. \tag{B-31}$$

At p = 0, w = 0 and

$$R_{p=0} = K. \tag{B-32}$$

The condition of cos w = 0 restricts w to

$$w = \frac{2n+1}{2}\,\pi \qquad n = 0, 1, 2, 3, \ldots \tag{B-33}$$

and, using L' Hospitals rule, the residue becomes

$$R_{\cos w = 0} = \frac{(K-1)\sin\frac{2n+1}{2}\,\pi U}{-\frac{2n+1}{2}\,\pi}\, e^{-\left(\frac{2n+1}{2}\pi\right)^2 Q} \tag{B-34}$$

$$n = 0, 1, 2, 3, \ldots$$

Then by summing the residues and substituting for the dimensionless variables, the solution of Fick's second law for the capillary reservoir technique becomes

$$C_A = C_r + (C_o - C_r)\frac{4}{\pi}\sum_{n=0}^{\infty}\frac{1}{2n+1}\, e^{-\left(\frac{2n+1}{2L}\pi\right)^2 pt} \sin\frac{(2n+1)\pi z}{2L}. \tag{B-35}$$

To make this solution usable it is integrated over the volume of the capillary; note that the final concentration measured is the average concentration, $\bar{C}_A$, and

$$\bar{C}_A = \frac{1}{V}\int_0^L \pi r^2 C_A\, dz. \tag{B-36}$$

Integration of Equation B-35 yields

$$C_A = C_r + \frac{1}{V}(C_o - C_r)\frac{4}{\pi}\int_0^L \sum_{n=0}^{\infty} \frac{\pi r^2}{2n+1} e^{-\left(\frac{2n+1}{2L}\pi\right)^2 Dt} \sin\frac{(2n+1)\pi z}{2L}\, dz \qquad (B\text{-}37)$$

or

$$\frac{\bar{C}_A - C_r}{C_o - C_r} = \frac{8}{\pi^2}\sum_{n=0}^{\infty}\frac{1}{(2n+1)^2} e^{-\left(\frac{2n+1}{2L}\pi\right)^2 Dt}. \qquad (B\text{-}38)$$

To facilitate the use of the above equation, Walls (23) has tabulated values of Q and $\frac{C_A - C_r}{C_o - C_r}$. He assumed values of Q ranging from 0. to 0.3600 in increments of 0.0001 and calculated the ratio of the concentrations. To apply Walls' results the concentration ratio is calculated from the data, the value of Q is determined from the table, and the diffusivity is calculated from

$$D = \frac{QL^2}{t}. \qquad (B\text{-}39)$$

The Boltzmann-Matano solution to Fick's second law will now be derived. This solution was presented by Boltzmann (4) and first used by Matano (17). The diffusion coefficient is not assumed constant and Fick's law takes the form

$$\frac{\partial C_A}{\partial t} = \frac{\partial}{\partial z}\left(D_{AB}\frac{\partial C_A}{\partial z}\right). \qquad (B\text{-}40)$$

The system under consideration consists of two regions which are to be connected at the beginning of the diffusion period. The initial conditions

are: $C_A = C_o'$ for $z < 0$ and $C_A = C_o'$ for $z < 0$. The boundary conditions are: $C_A = C_o$ for all t at one end of the diffusion couple and $C_A = C_o'$ for all t at the other end.

A new variable, y, is introduced which is a function of time and distance,

$$y = z\,t^{-1/2}. \tag{B-41}$$

Substitution of this variable into Equation B-40 reduces it to the ordinary differential equation

$$-\frac{y}{2}\frac{dC_A}{dy} = \frac{d}{dy}\left(D_{AB}\frac{dC_A}{dy}\right). \tag{B-42}$$

The above may be integrated once to yield

$$\left(D_{AB}\right)_{C''} = \frac{1}{\left(\frac{dC_A}{dy}\right)_{C_A''}}\int_{C_o}^{C_A''} y\,dC_A, \tag{B-43}$$

where C_A'' is any concentration between C_o and C_o'.

When the diffusion run is over the concentration profile (penetration curve) is determined for the entire length of the system and this data is used to solve for the diffusivity as a function of concentration. Since time is now a constant, Equation B-43 can be transformed to

$$\left(D_{AB}\right)_{C_A''} = -\frac{1}{2t}\left(\frac{dz}{dC_A}\right)_{C_A''}\int_{C_o}^{C_A''} z\,dC_A. \tag{B-44}$$

In order to implement the above result, the distance coordinate must be shifted such that the $z = 0$ plane is defined by

$$\int_{C_o}^{C_o'} z\, dC = 0. \qquad \text{(B-45)}$$

This is done by adjusting the zero plane until the positive and negative portions of the integral cancel each other. The diffusion coefficient is then found by determining the slope of the penetration curve and the value of the integral as functions of concentration. More complete descriptions of the Boltzmann-Matano method are given by Jost (15), Shewmon (21) and most modern metallurgy texts which deal with diffusion.

Ideal Solutions

In Chapter II Fick's second law was shown to be applicable to systems for which the specific volume follows a linear law, i.e., no change of volume on mixing. Consideration of Fick's second law as a generalized diffusion equation applicable at any temperature, pressure and composition allows its restriction to be stated as:

> Fick's second law is theoretically restricted to systems for which there is no change of volume on mixing for all temperature, pressure and composition. However, it may be applied, at a given temperature and pressure, to concentration intervals over which the specific volume of the solution is approximated by a linear law.

Stated mathematically this assumption, in the most general sense, is

$$\bar{V}_i = \underline{V}_i \quad \text{for all } T,\ P,\ X_i. \qquad \text{(B-46)}$$

The thermodynamic restrictions of the above condition will now be

investigated.

At constant composition the specific and partial molal Gibbs free energy are defined by

$$d\underline{G}_i = -\underline{S}_i\, dT + \underline{V}_i\, dP \tag{B-47}$$

and

$$d\overline{G}_i = -\overline{S}_i\, dT + \overline{V}_i\, dP. \tag{B-48}$$

The defining relationships for the fugacities are

$$\left(d\underline{G}_i\right)_{T,\,X} = \left(RT\, d\ln \underline{f}_i\right)_{T,\,X} \tag{B-49}$$

and

$$\left(dG_i\right)_{T,\,X} = \left(RT\, d\ln f_i\right)_{T,\,X} \tag{B-50}$$

Restriction of Equations B-47 and B-48 to constant temperature and substitution into Equations B-49 and B-50 leads to

$$\left(d\ln \underline{f}_i\right)_{T,\,X} = \left(\frac{1}{RT}\,\underline{V}_i\, dP\right)_{T,\,X} \tag{B-51}$$

and

$$\left(d\ln \overline{f}_i\right)_{T,\,X} = \left(\frac{1}{RT}\,\overline{V}_i\, dP\right)_{T,\,X}. \tag{B-52}$$

Subtraction of these results gives

$$\left(d\ln \frac{\overline{f}_i}{\underline{f}_i}\right)_{T,\,X} = \left(\frac{1}{RT}\,(\overline{V}_i - \underline{V}_i)\, dP\right)_{T,\,X}. \tag{B-53}$$

This is integrated from P = 0 where

$$\lim_{P \to 0} \frac{\overline{f}_i}{\underline{f}_i} = X_i$$

to some pressure, P, and

$$\int_{X_i}^{\frac{\bar{f}_i}{\underline{f}_i}} \left(d \ln \frac{\bar{f}_i}{\underline{f}_i} \right)_{T, X} = \frac{1}{RT} \int_{P=0}^{P} (\bar{V}_i - \underline{V}_i) \, dP_{T, X}. \tag{B-54}$$

The right side is zero by Equation B-46 and the left side integrated to

$$\ln \frac{\bar{f}_i}{\underline{f}_i} = \ln X_i \tag{B-55}$$

or

$$\bar{f}_i = X_i \underline{f}_i \, . \tag{B-56}$$

The above result is the Lewis and Randall fugacity rule and is the basic definition of an ideal solution.

Since Equation B-56 is applicable at all temperatures it may be differentiated with respect to temperature at constant pressure and composition to get

$$\left(\frac{d \ln \bar{f}_i}{dT} \right)_{P, X} = \left(\frac{d \ln \underline{f}_i}{dT} \right)_{P, X} \, . \tag{B-57}$$

The relationships

$$\left(\frac{d \ln \bar{f}_i}{dT} \right)_{P, X} = \frac{\overset{*}{H}_i - \bar{H}_i}{RT^2} \tag{B-58}$$

and

$$\left(\frac{d \ln \underline{f}_i}{dT} \right)_{P, X} = \frac{\overset{*}{H}_i - \underline{H}_i}{RT^2} \tag{B-59}$$

are substituted into Equation B-57 and

$$\underline{H}_i = \overline{H}_i. \tag{B-60}$$

Thus, the restriction that the change of volume on mixing is zero for all temperature, pressure and composition implies an ideal solution and the statement that Fick's second law is an ideal solution law is justified.

APPENDIX C

THERMODYNAMIC DATA

Elliott and Chipman (9) determined the electrode potential, with cadmium as the more electropositive component, for the cadmium-lead binary system from 400°C to 600°C. Their data were extrapolated to 350°C and were used in this work. The relationship between the Gibbs free energy and the electrode potential, E, is given by

$$\Delta G_{Cd} = RT \ln a_{Cd} = -2FE \qquad (C\text{-}1)$$

where F is the Faraday constant.

From the extrapolated data the values of $\ln \gamma$ were calculated by

$$\ln \gamma_{Cd} = \ln \left(\frac{a}{X}\right)_{Cd} = -\frac{2}{RT} \int E - \ln X_{Cd}. \qquad (C\text{-}2)$$

These results were plotted versus $(1 - X_{Cd})^2$ and are shown in Figure C-1. From the derivatives of this curve the thermodynamic factor was calculated by

$$\frac{d \ln a_{Cd}}{d \ln X_{Cd}} = 1 - X_{Cd} X_{Pb} \frac{d \ln \gamma_{Cd}}{d(1-X_{Cd})^2} . \qquad (C\text{-}3)$$

The results are shown in Figure C-2.

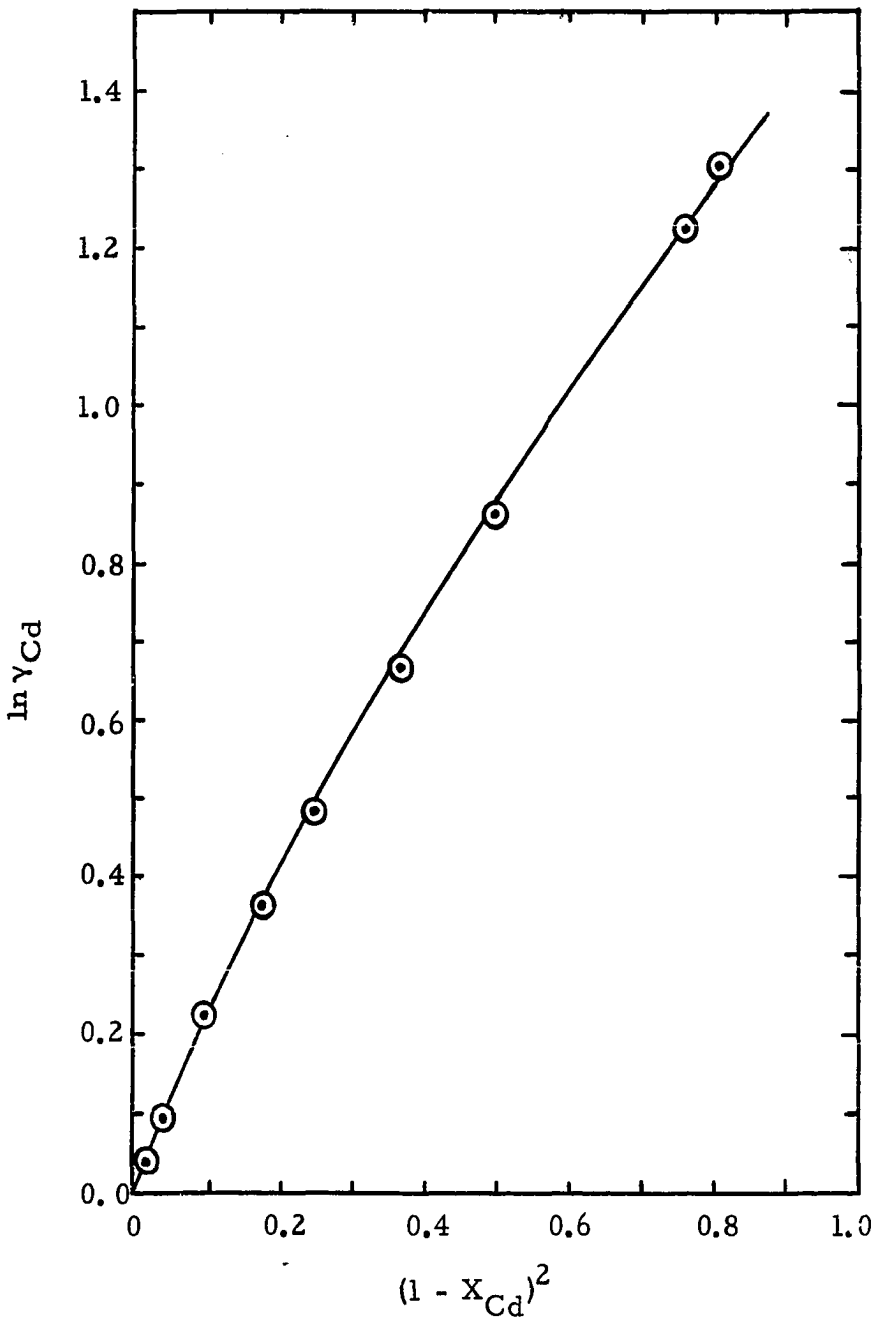

Figure C-1. Elliott and Chipman's Thermodynamic Data; Extrapolated to 350°C

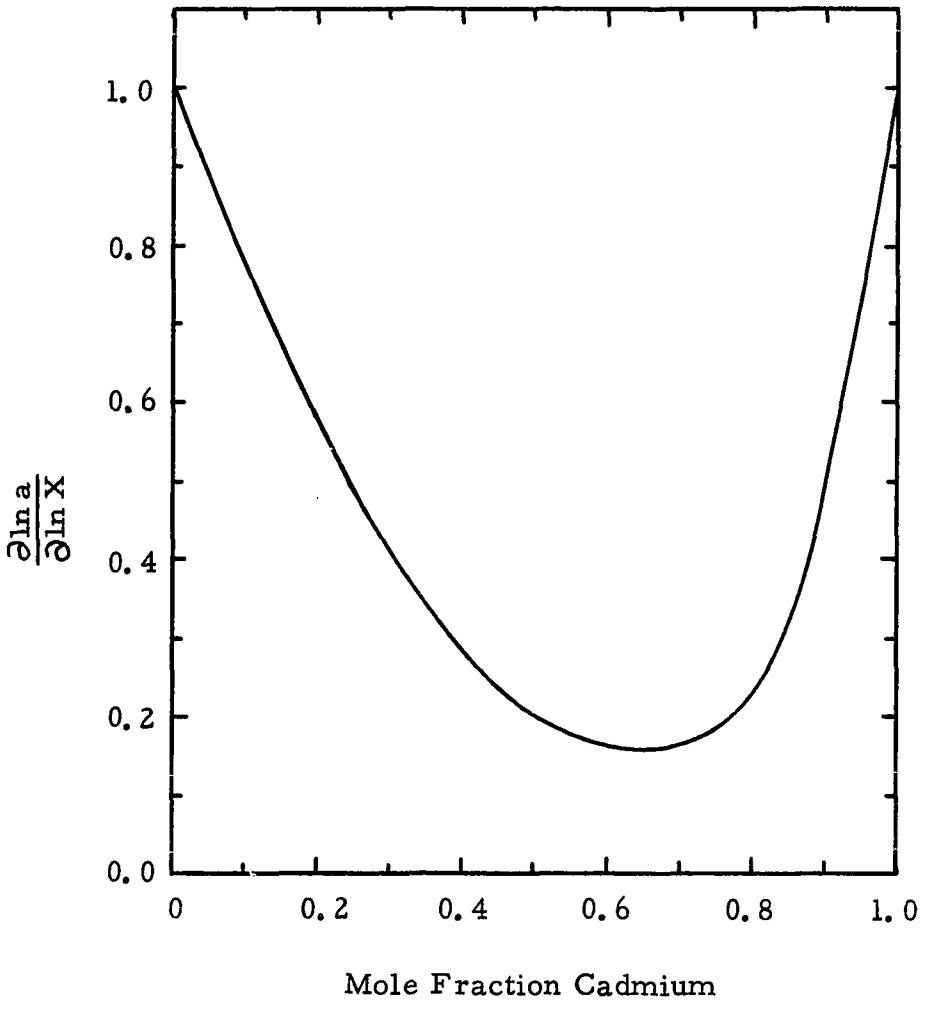

Figure C-2. Thermodynamic Factor as a Function of Concentration at 350°C

APPENDIX D

ISOTOPE ANALYSIS

The lead 210 was purchased from the Radiochemical Centre, Amersham, Buckinghamshire, England, as lead nitrate in 2.5N nitric acid. Pb-210 does not have a characteristic gamma spectrum because it and its decay products give many low energy gamma rays. The gamma spectrum was obtained to determine if any impurities were present. This spectrum is given in Figure D-1, and, as can be seen, no impurities were detected.

The cadmium 115m was purchased from the Union Carbide Corporation, Nuclear Division, Oak Ridge National Laboratory as cadmium nitrate in 0.84N nitric acid. Previously Mirshamsi (18) experienced considerable trouble with cadmium isotopes from Oak Ridge. Some of his shipments contained a considerable amount of silver 110m. The gamma spectrum of the Cd-115m used in this work is given in Figure D-2, and has the same energy peaks as the spectrum given by Heath (14). No impurities were detected.

The gamma spectra were run on an automated gamma spectrum analyzer at the University of Oklahoma Reactor Laboratory under the direction of Dr. A. E. Wilson.

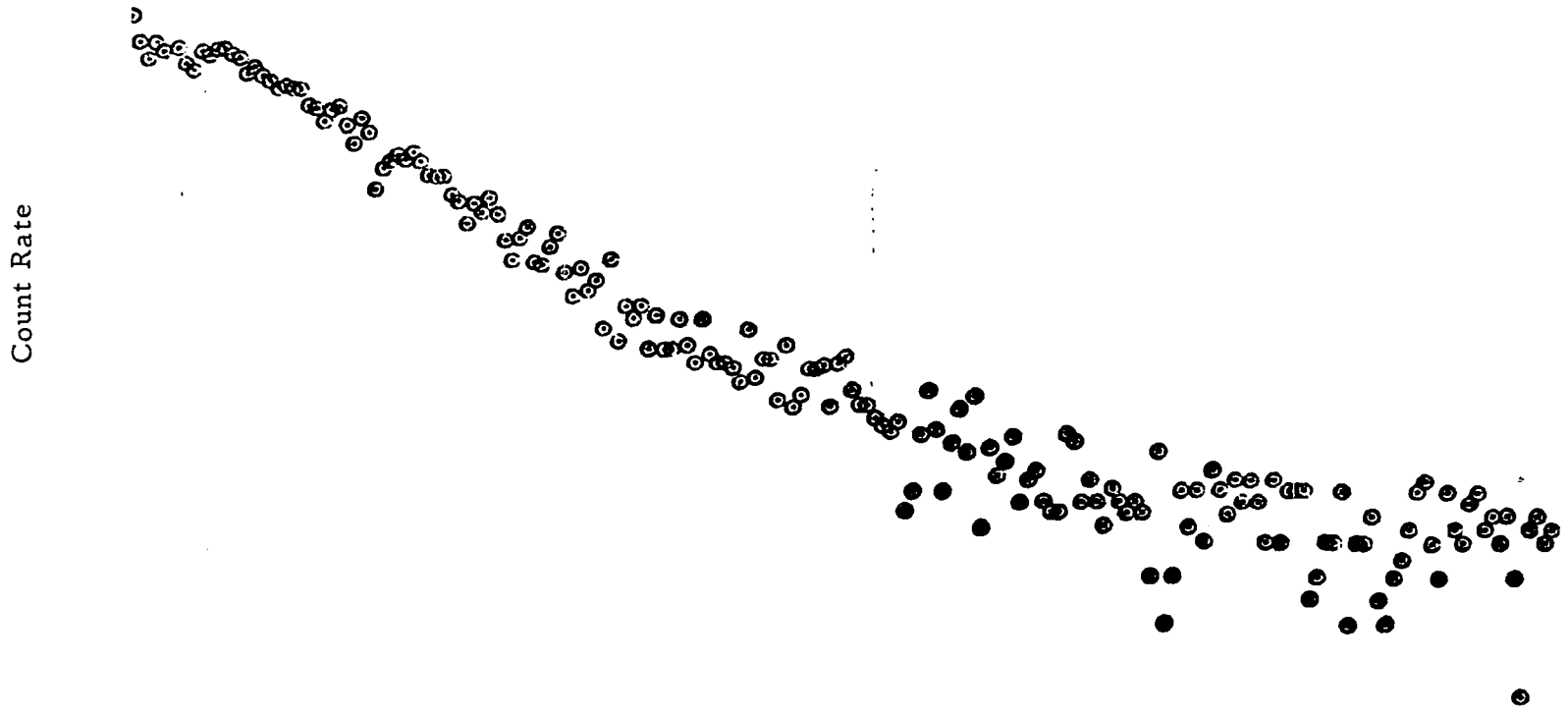

Figure D-1. 0-1 mev Gamma Spectrum for Lead 210

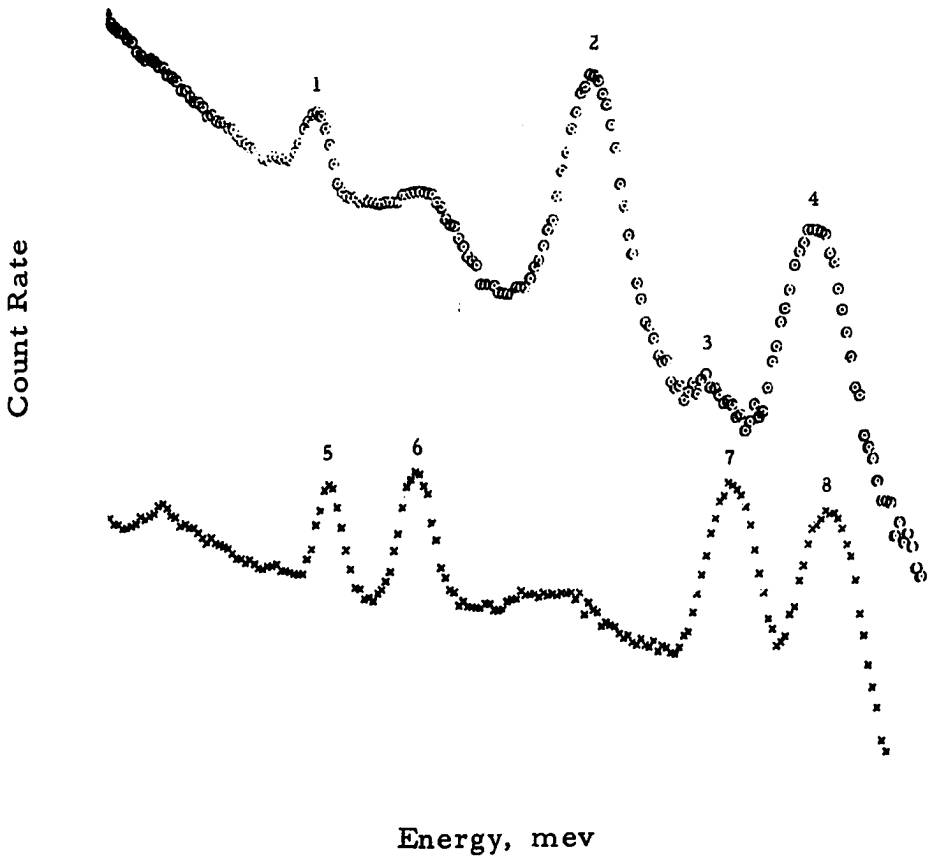

Figure D-2. Cadmium 115m Gamma Spectrum

⊙ - Cadmium Spectrum
1. 0.485 mev
2. 0.935 mev
3. 1.112 mev
4. 1.285 mev

x - Calibration Spectra
5. Na^{22}, 0.511 mev
6. Cs^{137}, 0.662 mev
7. Co^{60}, 1.17 mev
8. Co^{60}, 1.33 mev

APPENDIX E

NEGATIVE PARTIAL MOLAL VOLUMES

The partial molal volume of component i in a mixture is defined as

$$\bar{V}_i = \left(\frac{\partial V}{\partial N_i}\right)_{N,\, P,\, N_j} . \qquad \text{(E-1)}$$

When a small amount of component B is added to a mixture of A and B and the final volume is less than the original volume of the mixture, component B has a negative partial molal volume, i. e., the right side of Equation E-1 is negative. Several systems (2, 23) have been reported where the partial molal volume of one component is negative over a portion of the composition range. The characteristics of such a binary system will be used in this section to demonstrate the need for utilization of the proper diffusion equations.

Consider a binary solution of components A and B having the specific volume versus mole fraction relationship shown in Figure E-1. (This binary solution is totally fictitious.) Inspection of the curve indicates that $\bar{V}_B$ is zero at $X_A = 0.9$ and negative for $0.9 < X_A < 1.0$.

It is now assumed that, whether the mixture is gas, liquid or

solid, diffusion data can be obtained similar to the penetration curve for two semi-infinite solid rods. The initial conditions are shown in Figure E-2.

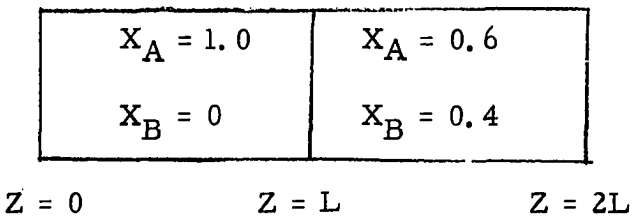

Figure E-2. Diffusion Couple

After diffusion has proceeded for a specified time the mole fraction of A will be 1.0 at z = 0 and will decrease in a regular manner to a value of 0.6 at 2L. Similarly, $X_B = 0$ at 3 = 0 and 0.4 at 2L obeying the rule $X_A + X_B = 1$. The penetration curve, plotted as mole fraction versus distance, then could take the form shown in Figure E-3. From the penetration curve in Figure E-3 and the specific volume data in Figure E-1, the concentration versus distance relationship is determined and illustrated in Figure E-4. A maximum exists at $X_A = 0.9$ and diffusion actually occurs against the concentration gradient of A.

Assuming that the interface defined by

$$\int_{C_o}^{C_o'} z \, dC_A = 0 \qquad \text{(E-2)}$$

could logically be located, the Boltzmann-Matano solution still gives erroneous results. (See Appendix B for discussion of Boltzmann-Matano method.) Since

$$(D_{AB})_{C_A''} = -\frac{1}{2t}\left(\frac{\partial z}{\partial C_A}\right)_{C_A''} \int_{C_o}^{C_A''} z\, dC_A \qquad \text{(E-3)}$$

and $\frac{\partial C_A}{\partial z} = 0$ at $X_A = 0.9$, D_{AB} must go to infinity at that point. Furthermore, D_{AB} will be minus infinity on one side of $X_A = 0.9$ and plus infinity on the other side. It could be argued that the integral in Equation E-3 should be zero at $X_A = 0.9$, but this leads to two coordinate systems for the analysis.

The solution to Fick's second law used in this work, Equation 26, also fails since it restricts diffusion to the opposite direction of the concentration gradient. Thus, it would predict that component A is diffusing, in both directions, away from the point in space where $X_A = 0.9$.

The case of negative partial molal volumes is extreme but does point out the need for care and forthought before applying the diffusion equation to experimental data.

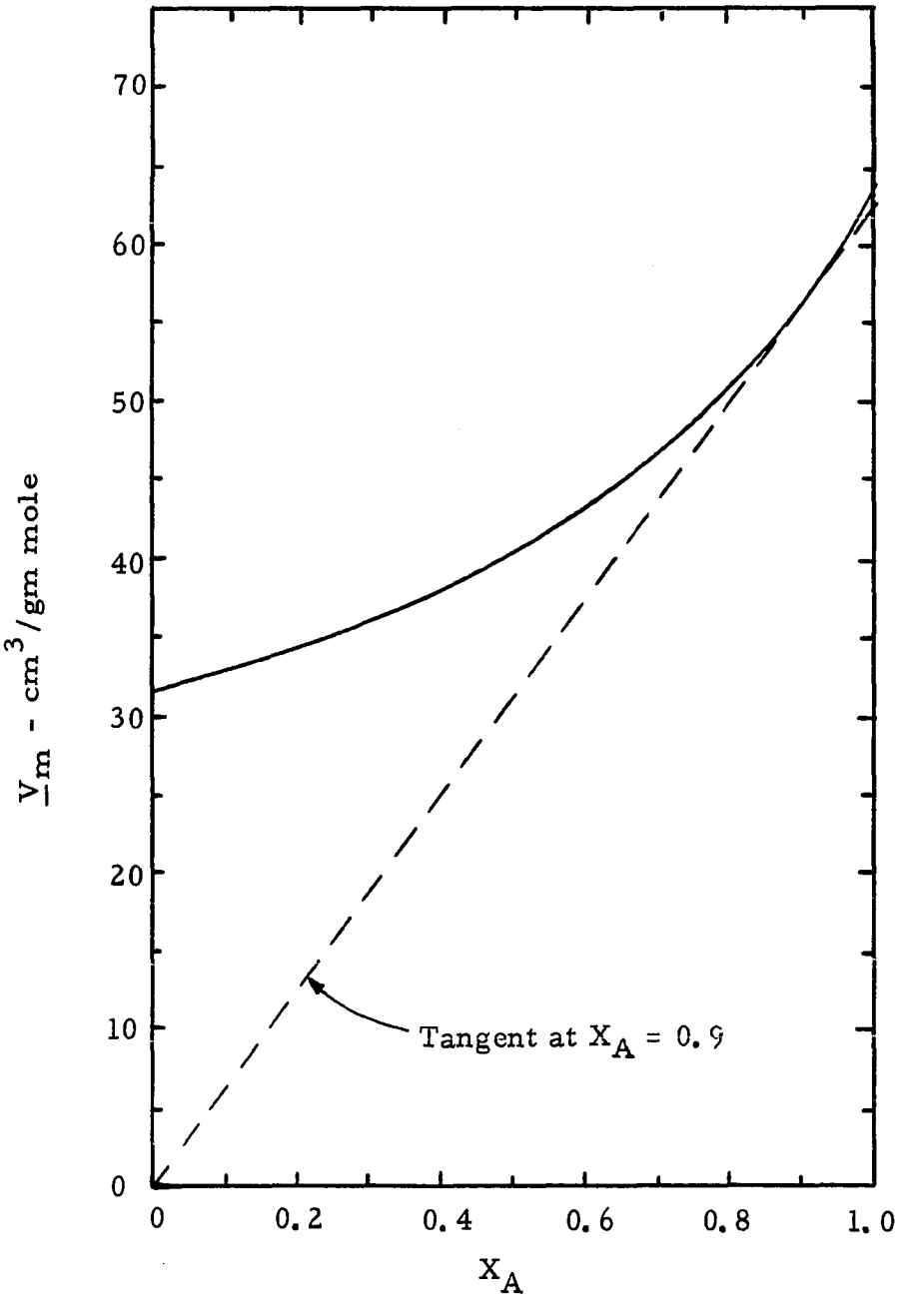

Figure E-1. Specific Volume--Concentration Relationship for a Hypothetical Binary Solution

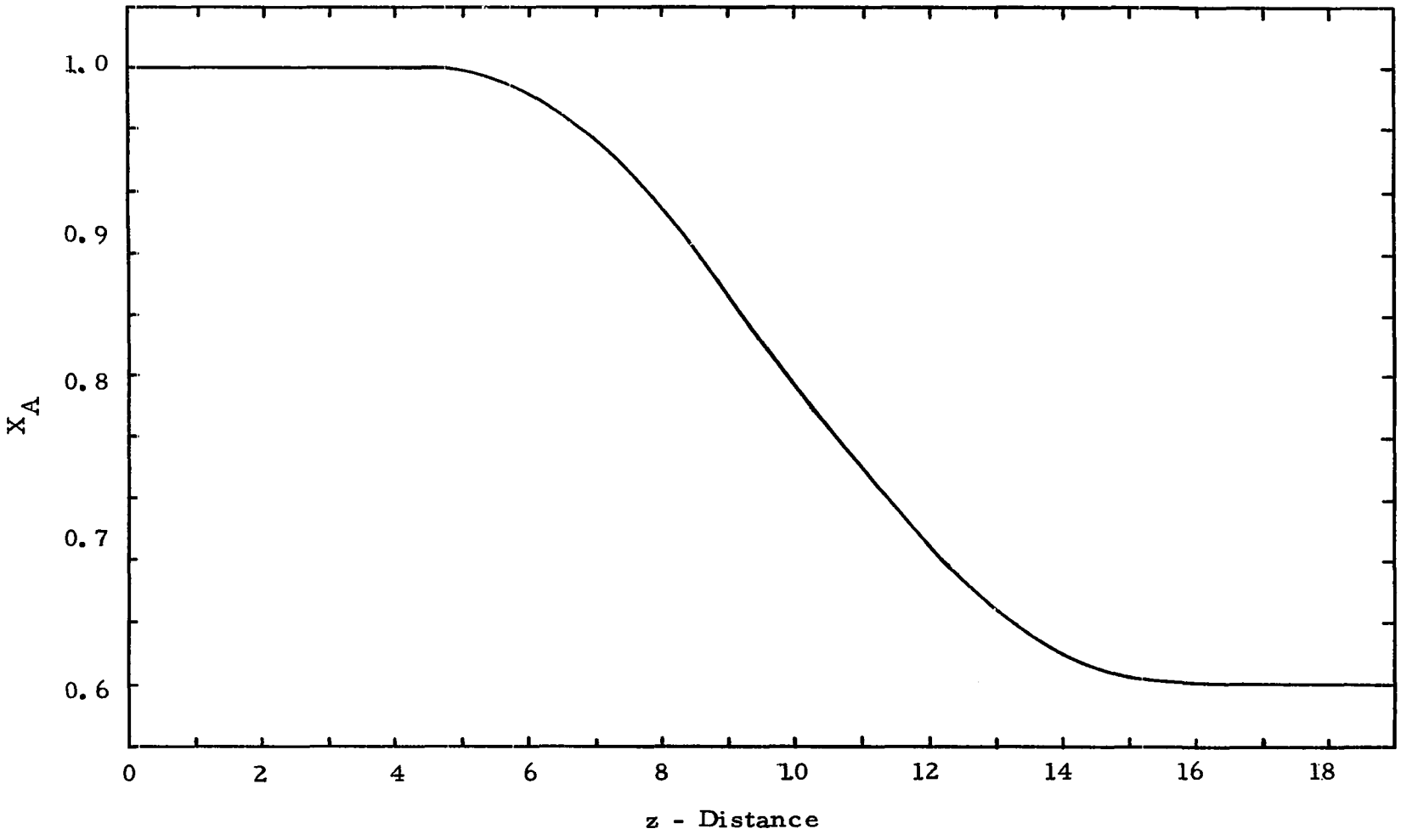

Figure E-3. Mole Fraction Penetration Curve

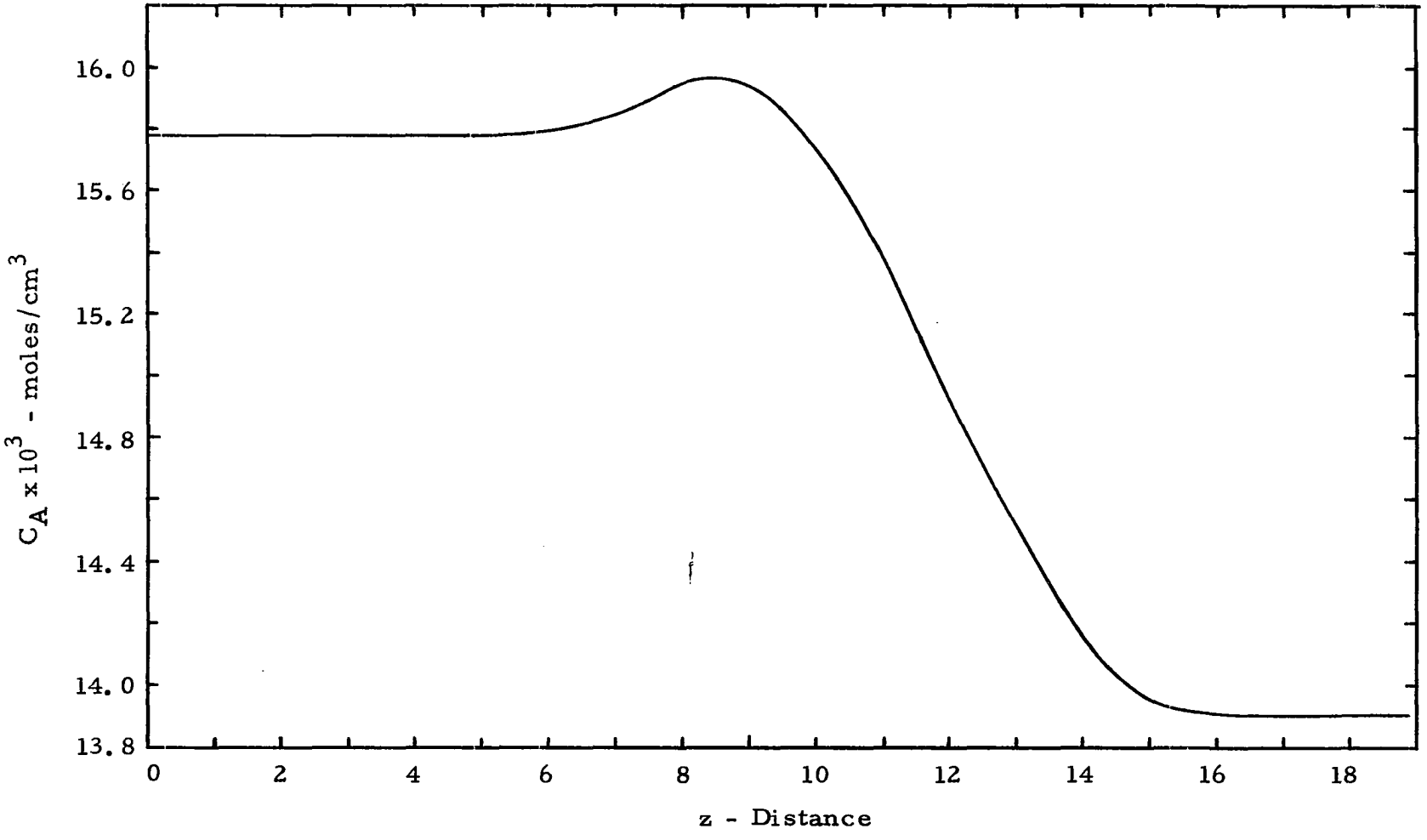

Figure E-4. Concentration Penetration Curve

TABLE F-1

SELF DIFFUSION OF PURE LEAD AT 400°C

Capillary number	Length inches	Time sec	$C_o - C_r$ cpm	$C_f - C_r$ cpm	$\frac{C_f - C_r}{C_o - C_r}$	Q	$D \times 10^5$ cm^2/sec
1	.968	36000	5038	2992	.5939	.1296	2.12
2	1.000	36000	4959	2894	.5836	.1362	2.44
3	.985	36000	5031	2686	.5339	.1707	2.97
4	.967	36000	4977	2978	.5984	.1267	2.12
5	.997	36000	5086	2996	.5912	.1313	2.34
6	1.005	36000	5078	3015	.5937	.1297	2.35
7	.953	36000	4635	2750	.5928	.1302	2.12
8	.950	36000	4718	2460	.5596	.1524	2.46
9	.993	36000	5061	2958	.5846	.1356	2.40

TABLE F-2

SELF DIFFUSION OF LEAD

Capillary number	Cd mass percent	Length inches	Time sec	$C_o - C_r$ cpm	$C_f - C_r$ cpm	$\frac{C_f - C_r}{C_o - C_r}$	Q	$D \times 10^5$ cm^2/sec
16	11.7	1.027	28800	1577.8	1090.8	.6557	.0931	2.24
17	11.7	1.034	28800	1616.3	1010.7	.6253	.1103	2.68
18	11.7	1.036	28800	1658.7	1007.8	.6076	.1209	2.95
19	11.7	.987	30600	1502.1	954.6	.6355	.1043	2.18
20	11.7	.932	30600	1450.8	845.9	.5830	.1366	2.54
21	11.7	.969	30600	1573.9	980.7	.6231	.1116	2.24
44	30.7	.996	25200	1007.8	654.1	.6490	.0967	2.49
45	30.7	1.007	25200	985.9	645.2	.6544	.0938	2.43
46	30.7	.987	25200	915.6	625.1	.6482	.0972	2.42
47	30.7	.982	25200	916.7	634.6	.6923	.0744	1.84
48	30.7	1.000	25200	898.4	596.0	.6634	.0889	2.27
49	30.7	1.240	25200	1112.0	771.2	.6935	.0738	2.86
50	30.7	1.240	25200	1056.8	768.8	.7275	.0583	2.30
51	30.7	1.240	25200	1147.9	847.8	.7386	.0537	2.11
221	70.0	1.040	25920	25553.8	17184.2	.6725	.0842	2.27
222	70.0	1.040	25920	25666.9	17099.4	.6662	.0875	2.36
223	70.0	1.040	25920	25976.0	17007.6	.6547	.0936	2.52

TABLE F-3

SELF DIFFUSION OF CADMIUM

Capillary number	Cd mass percent	Length inches	Time sec	$C_o - C_r$ cpm	$C_f - C_r$ cpm	$\frac{C_f - C_r}{C_o - C_r}$	Q	$D \times 10^5$ cm^2/sec
52	100	1.002	21600	9048.2	6413.8	.7088	.0606	2.07
53	100	1.002	21600	9813.1	6492.3	.6616	.0899	2.79
54	100	1.002	21600	8803.7	5759.3	.6542	.0939	2.92
55	100	1.002	30000	9682.5	6397.0	.6607	.0904	2.02
56	100	1.002	30000	9118.3	5633.2	.6178	.1147	2.57
57	100	1.002	30000	9399.6	6127.2	.6518	.0952	2.13
122	70.0	1.002	29940	7934.4	4696.2	.5920	.1308	2.93
123	70.0	1.002	29940	7982.7	4948.6	.6199	.1135	2.54
124	70.0	1.002	29940	7867.6	4800.8	.6120	.1193	2.67
153	23.9	1.002	29520	4551.7	2829.8	.6217	.1124	2.56
154	23.9	1.002	29520	4710.0	2655.7	.5649	.1487	3.38
155	23.9	1.002	29520	4586.6	2924.4	.6376	.1031	2.34

TABLE F-4

MUTUAL DIFFUSION; Pb-210 TRACER

Capillary number	Length inches	Time sec	C_o cpm*	C_f cpm*	C_r cpm*	$\frac{C_f - C_r}{C_o - C_r}$	Q	D x 10^5 cm^2/sec
8.9 mass % Cd; capillary 6.08% Cd; reservoir 11.81% Cd								
10	.999	35880	1723	1614	1577	.3039	<.36	<10
11	.979	35880	1805	1684	1577	.4693	.220	3.83
12	.980	35880	1810	1693	1577	.5202	.1810	3.13
14	1.045	43920	1845	1706	1577	.7630	.0441	.71
15	1.053	43920	1733	1633	1577	.3613	.3276	5.32
14.6 mass % Cd; capillary 11.81% Cd; reservoir 17.44% Cd								
24	1.021	21600	1557.2	1491.6	1433.7	.4689	.2223	6.92
25	.979	21600	1554.7	1500.7	1431.4	.5615	.1511	4.32
26	.963	21600	1533.4	1485.0	1411.8	.6023	.1243	3.44
28	.936	29100	1502.5	1436.4	1383.3	.4454	.2431	4.72
29	.967	23400	1470.6	1414.5	1409.4	.5191	.1819	4.69
26.4 mass % Cd; capillary 22.22% Cd; reservoir 30.65% Cd								
37	.947	21600	1272	1067	990	.2730	<.36	<10
38	1.047	21600	1193	1062	990	.3547	.3350	11.61
39	.966	21600	1223	1044	990	.2361	<.36	<10
40	.974	21600	1278	1154	990	.5694	.1457	4.13
41	.975	21600	1271	1152	990	.5730	.1432	4.07
42	1.036	21600	1260	1144	990	.5704	.1450	4.65

TABLE F-4--Continued

Capillary number	Length inches	Time sec	C_o cpm*	C_f cpm*	C_r cpm*	$\frac{C_f - C_r}{C_o - C_r}$	Q	$D \times 10^5$ cm^2/sec
50.6 mass % Cd; capillary 47.03% Cd; reservoir 54.11% Cd								
170	1.040	23340	52941.1	51100.5	42065.1	.8308	.0225	.67
171	1.040	23340	52888.9	51490.0	42115.3	.8702	.0132	.39
172	1.040	23340	53603.4	51490.0	41867.3	.8199	.0255	.76
70.0 mass % Cd; capillary 68.00% Cd; servoir 72.02% Cd								
211	1.040	43200	23263.8	22700.4	21540.8	.6711	.0850	1.37
212	1.040	43200	23411.3	22915.9	21973.8	.6544	.0933	1.51

*These values are cpm per unit length for the glass capillaries (numbers 10-15 and 37-42)

TABLE F-5

MUTUAL DIFFUSION; Cd-115m TRACER

Capillary number	Time sec	C_o cpm	C_f cpm	C_r cpm	$\frac{C_f - C_r}{C_o - C_r}$	Q	D x 10^5 cm^2/sec
11.9 mass % Cd; capillary 7.85% Cd; reservoir 15.96% Cd							
140	30360	1576.7	1994.5	2945.4	.6952	.0730	1.61
142	30360	1593.2	2051.9	2976.2	.6683	.0864	1.91
143	25800	1546.4	1960.7	2936.1	.7019	.0698	1.82
145	25800	1538.4	2068.5	3022.5	.6428	.1002	2.61
146	25800	1555.2	2039.3	2956.5	.6545	.0938	2.44
19.9 mass % Cd; capillary 15.96% Cd; reservoir 23.92% Cd							
147	23340	2945.4	3255.6	4551.7	.8069	.0293	.843
149	23340	2976.2	3379.2	4586.6	.7498	.0492	1.415
151	24120	3022.5	3412.0	4710.0	.7692	.0418	1.163
152	24120	2956.5	3357.0	4586.6	.7543	.0474	1.319
33.9 mass % Cd; capillary 29.51% Cd; reservoir 38.32% Cd							
156	23280	5106.3	5213.3	6466.5	.9213	.0049	.141
157	23280	5214.0	5681.2	6640.0	.6724	.0843	2.431
158	23280	4987.3	5373.5	6393.7	.7254	.0592	1.707
42.5 mass % Cd; capillary 38.32% Cd; reservoir 46.70% Cd							
159	21900	6466.5	6532.6	7324.4	.9230	.0046	.14
160	21900	6640.0	6718.0	7581.8	.9172	.0054	.17
161	21900	6393.4	6598.2	7340.5	.7838	.0367	1.17

TABLE F-5--Continued

Capillary number	Time sec	C_o cpm	C_f cpm	C_r cpm	$\frac{C_f - C_r}{C_o - C_r}$	Q	D x 10^5 cm^2/sec
50.4 mass % Cd; capillary 46.70% Cd; reservoir 54.08% Cd							
163	22080	7581.8	7752.5	9006.9	.8802	.0113	.34
164	22080	7340.5	7367.6	8802.4	.9815	.0002	.006
70.0 mass % Cd; capillary 68.02 % Cd; reservoir 71.99% Cd							
116	21840	8743.8	8938.2	8993.4	.2212	<.36	< 10
117	21840	8749.7	9081.2	9192.2	.2508	<.36	< 10
118	21840	8833.5	9003.1	9238.7	.5814	.1376	4.40
120	25380	8972.8	9081.2	9192.2	.5059	.1921	5.28

TABLE F-6

LEAD SELF DIFFUSION-FUNCTION OF CONCENTRATION INTERVAL

Capillary number	Time sec	$C_o - C_r$ cpm	$C_f - C_r$ cpm	$\frac{C_f - C_r}{C_o - C_r}$	Q	$D \times 10^5$ cm^2/sec
capillary 60.0 mass % Cd; reservoir 80.0% Cd; interval 20.04%						
181	28920	31683.5	19960.9	.6300	.1075	2.59
capillary 63.9 mass % Cd; reservoir 76.1% Cd; interval 12.28%						
185	32880	27715.8	17884.6	.6453	.0988	2.10
186	32880	27832.6	17286.1	.6211	.1128	2.39
187	32880	28017.1	18633.8	.6651	.0881	1.87
capillary 66.0 mass % Cd; reservoir 74.0% Cd; interval 8.00%						
191	21600	24734.7	18400.2	.7439	.0515	1.66
192	21600	24493.7	16340.6	.6671	.0870	2.81
194	21600	24986.6	19163.4	.7669	.0427	1.38
capillary 68.0 mass % Cd; reservoir 72.0% Cd; interval 4.02%						
198	33000	22005.8	14009.2	.6366	.1037	2.19
199	33000	22224.1	13949.4	.6277	.1089	2.30

TABLE F-7

CADMIUM SELF DIFFUSION-FUNCTION OF CONCENTRATION INTERVAL

Capillary number	Time sec	$C_o - C_r$ cpm	$C_f - C_r$ cpm	$\frac{C_f - C_r}{C_o - C_r}$	Q	$D \times 10^5$ cm^2/sec
capillary 59.9 mass % Cd; reservoir 80.0% Cd; interval 19.96%						
58	21600	7517.0	5196.9	0.6914	0.0748	2.32
59	21600	6720.4	4726.7	0.7033	0.0691	2.15
60	21600	6867.0	4882.6	0.7110	0.0656	2.04
capillary 64.2 mass % Cd; reservoir 75.8% Cd; interval 11.62%						
76	21900	8384.8	5794.5	0.6911	0.0749	2.30
77	21900	8599.3	5891.9	0.6852	0.0778	2.38
78	21900	8726.8	5977.6	0.6850	0.0779	2.39
capillary 66.0 mass % Cd; reservoir 74.0% Cd; interval 7.95%						
88	31800	8953.5	5621.9	0.6279	0.1087	2.29
89	31800	8856.0	5696.9	0.6433	0.0999	2.11
90	31800	9209.7	5701.9	0.6133	0.1174	2.48
capillary 68.0 mass % Cd; reservoir 72.0% Cd; interval 3.98%						
110	26220	8923.4	5491.2	0.6154	0.1162	2.97
111	26220	8777.8	5634.8	0.6419	0.1007	2.58
112	26220	8954.4	5529.8	0.6176	0.1149	2.94
113	26220	9269.6	6123.2	0.6606	0.0905	2.61
114	26220	9250.1	6333.2	0.6847	0.0781	2.02
115	26220	9282.7	6093.4	0.6564	0.0927	2.67

TABLE F-8

MUTUAL DIFFUSION-FUNCTION OF CONCENTRATION INTERVAL; Pb-210 TRACER

Capillary number	Time sec	C_o cpm	C_f cpm	C_r cpm	$C_f - C_r$ / $C_o - C_r$	Q	D x 10^5 cm^2/sec
capillary 66.0 mass % Cd; reservoir 74.0%; interval 8.00%							
195	22980	26822.0	25569.5	20369.6	.8059	.0296	.90
196	22980	27153.4	25683.5	20198.8	.7886	.0351	1.07
197	22980	27393.0	25824.1	20649.2	.7674	.0425	1.29
capillary 63.9 mass % Cd; reservoir 76.1%, interval 12.28%							
188	27600	27881.3	25192.1	19052.9	.6954	.0729	1.84
190	27600	28246.4	25508.4	19105.8	.7005	.0704	1.78

TABLE F-9

MUTUAL DIFFUSION-FUNCTION OF CONCENTRATION INTERVAL; Cd-115m TRACER

Capillary number	Time sec	C_o cpm	C_f cpm	C_r cpm	$\frac{C_f - C_r}{C_o - C_r}$	Q	D x 10^5 cm^2/sec
capillary 59.9 mass % Cd; reservoir 80.1% Cd; interval 20.12%							
64	23400	8497.1	8895.6	10102.9	.7518	.0484	1.39
65	23400	8592.1	9071.6	10253.2	.7113	.0655	1.88
66	23400	8573.0	8906.1	10340.9	.8116	.0279	0.80
67	21720	8652.7	9356.8	10102.9	.5145	.1854	5.73
68	21720	8663.1	9698.3	10253.2	.3490	.3416	10.56
69	21720	8683.8	9530.6	10340.9	.4890	.2056	6.35
capillary 64.2 mass % Cd; reservoir 75.8% Cd; interval 11.65%							
82	22500	8512.1	9125.1	9686.4	.4780	.2147	6.40
83	22500	8641.6	9274.7	9793.3	.4503	.2386	7.12
84	22500	8417.5	8991.5	9985.9	.6340	.1052	3.14
85	21600	8790.7	9268.8	9686.4	.4774	.2152	6.69
86	21600	9105.0	9666.6	9793.3	.1841	<.36	<10
87	21600	9092.7	9511.2	9985.9	.5315	.1725	5.36
capillary 66.0 mass % Cd; reservoir 74.0% Cd; interval 7.94%							
94	23760	8459.2	8504.0	9674.5	.9631	.0011	.003
95	23760	8399.8	8796.6	9771.4	.7118	.0652	.19
97	26340	8653.2	9290.4	9674.6	.3440	.3474	9.20
98	26340	8947.9	9413.2	9771.4	.4350	.2525	6.69
99	26340	8781.1	9206.3	9647.3	.5091	.1895	5.02